AIDS TO THE STUDY OF EXAMIN

INTERMEDIATE CH

(C. U. Questions with Answers)

An Experienced Professor

Revised by

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Q. 1. *Explain and illustrate the law of equivalent proportions. What is meant by the term equivalent weight of an element and how is it related to its atomic weight?*

Describe an experiment to determine the equivalent weight of copper. What further facts and reasonings are required to fix its atomic weight?

Ans. The law of equivalent proportions is stated thus :—

When elements combine among themselves, they do so in the ratio of their equivalent weights or in the ratio of multiples of these equivalents.

The law can be illustrated by taking into consideration the weights in grams in which several elements individually combine with chemical equivalent of a particular element, say oxygen, since most of the elements are known to form oxides. We shall take into consideration the different weights in grams of several elements which are capable of combining with 8 grams of oxygen, its equivalent weight. It is known from analysis that

8 grams of oxygen combine with 1 gram of hydrogen
20 grams of calcium
35·5 grams of chlorine
12 grams of magnesium.

The law states that the elements on the right-hand side shall combine, if they combine at all, with one another in proportions of the weights mentioned or in the ratio of simple multiples of those weights.

For example :

20 grams of calcium shall combine with
35·5 grams of chlorine
19 grams of fluorine
1 gram of hydrogen, etc.
12 grams of magnesium shall combine with
35·5 grams of chlorine
19 grams of fluorine, etc.

But the weights of elements which combine with 1 part by weight of hydrogen or 8 parts by weight of oxygen are called the equivalent weights of those elements. Thus it is found that the elements like calcium, magnesium, etc., combine with elements like chlorine, fluorine, etc., in the proportions of their equivalent weights.

Equivalent weight of an element is that weight of it which can combine with or displace 1 part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine, etc. Thus, equivalent weight of an element

$$= \frac{\textit{Weight of the element}}{\textit{Weight of hydrogen}}$$

(combined with or displaced by the weight of the element taken).

Thus, equivalent weight is a mere number. *Gram equivalent* of an element is the equivalent weight of the element expressed in gram. It is known from experiment that 35·5 grams of chlorine combine with one gram of hydrogen. Therefore, 35·5 is the equivalent weight of chlorine.

Atomic weight of an element is related to equivalent weight of that element in such a way that $\frac{\text{Atomic weight}}{\text{Equivalent weight}}$ = a whole number which expresses the valency of the element.

Thus, Equivalent weight × valency
= Atomic weight.

The equivalent weight of copper is determined by the following experiment :

A porcelain crucible with its lid is taken. It is thoroughly cleansed, dried, heated on a clay-pipe triangle for about half an hour, cooled in a desiccator and weighed in a chemical balance. Heating, cooling and weighing is continued till the weight of the crucible with lid becomes *constant.* Next a piece of *pure* copper wire is taken in the crucible and after placing the lid in position, the whole is weighed again in the chemical balance. The difference in the two weighings will give the weight of copper taken. Now, the crucible is placed on an asbestos board, the lid is pushed aside a little and conc. nitric acid is added to copper drop by drop till the metal is completely dissolved. The crucible is to be kept nearly covered during the reaction. The crucible is next placed on a water bath after pushing the lid aside and the solution is evaporated slowly, taking care that there is no loss of solution by spirting. The green residue left in the crucible is of copper nitrate. Next the crucible is strongly heated over a Bunsen flame by placing it on a clay-pipe triangle with the lid pushed aside a little at first and then covered completely till the copper nitrate is completely converted into black copper oxide. The crucible with the lid is then cooled in a desiccator and weighed again. The processes of heating, cooling and weighing are continued till the final weight is constant.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + N_2O_4$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

Calculations :—

Let the weight of the crucible and lid $= w_1$ grams.
The weight of the crucible and lid + copper $= w_2$ grams.
∴ wt of copper taken $= (w_2 - w_1)$ grams.
Last weight of the crucible and lid + copper oxide $= w_3$ grams.
∴ wt. of oxygen combined with the given weight of copper $= (w_3 - w_2)$ grams.

Thus, $(w_3 - w_2)$ grams of oxygen has combined with $(w_2 - w_1)$ grams of copper to form copper oxide.

Therefore, 8 grams of oxygen will combine with

$\frac{w_2 - w_1}{w_3 - w_2} \times 8$ grams of copper. Hence, by definition, the

equivalent weight of copper $= \frac{w_2 - w_1}{w_3 - w_2} \times 8.$

The facts that are to be known are (1) Dulong and Petit's rule, *viz.*, Atomic weight of an element × its specific heat = 6·4 (approx.) from which, by knowing the specific heat of the element by actual determination, the approximate atomic weight of the element can be found ; (2) the relationship, *viz.*, equivalent weight × valency = Atomic weight. Thus, by dividing the approximate atomic weight as found by the application of Dulong and Petit's rule by the equivalent weight as determined experimentally very accurately, we shall get a number which, if fractional, is to be rounded off to the nearest whole number. This is the valency of the element. Next by multiplying the equivalent weight determined with accuracy by the valency found as above, we can determine the atomic weight of the element, copper.

Q. 2. *Calculate the volume of hydrogen at 27°C. and 750 mm. pressure that will be produced in each of the following cases by the decomposition of 5·4 grams of water when (a) water is acted upon by metallic sodium, (b) water reacts with calcium hydride, (c) water is passed in the form of steam over red-hot iron.*

What is **nascent** *hydrogen ? Describe an experiment to prove that it is a more powerful reducing agent than ordinary hydrogen gas.*

Ans. (*a*) From the equation

$$\underset{2\times 18}{2Na + 2H_2O} = 2NaOH + \underset{2}{H_2}$$

We know that 2 × 18 grams of water give rise to 2 grams of hydrogen when acted upon by sodium. But 2 grams of hydrogen occupy 22·4 litres at N.T.P. since molecular weight of any gas expressed in grams occupy 22·4 litres at N.T.P. Therefore, 2 × 18 grams of water give rise to 22·4 litres of hydrogen at N.T.P. in this case.

Hence 5·4 grams of water will give rise to $\frac{22{\cdot}4}{2\times 18} \times 5{\cdot}4$ or 3·36 litres at N.T.P.

Let V be the volume occupied by this hydrogen at 27°C. and 750 mm. pressure.

Then by Boyle's and Charles' Laws, we have

$$\frac{3{\cdot}36 \times 760}{273} = \frac{V \times 750}{273 + 27}$$

$$\therefore \quad V = \frac{3{\cdot}36 \times 760 \times 300}{273 \times 750} = 3{\cdot}74 \text{ (approx.) litres.}$$

(*b*) From the equation

$$\underset{}{CaH_2} + \underset{2 \times 18}{2H_2O} = Ca(OH)_2 + \underset{2 \times 2}{2H_2}$$

We know that 2 × 18 grams of water give rise to 2 × 2 grams of hydrogen. But 2 grams of hydrogen occupy 22·4 litres at N.T.P., since molecular weight of any gas expressed in grams occupy 22·4 litres at N.T.P. Thus, 2 × 18 grams of water in this case give rise to 2 × 22·4 litres at N.T.P.

Therefore, 5·4 grams of water will produce $\frac{2 \times 22{\cdot}4}{2 \times 18} \times 5{\cdot}4$ or 6·72 litres at N.T.P, Thus, the volume of hydrogen in this case is double the volume of hydrogen obtained in case (*a*).

The volume of hydrogen at 27°C., and 750 mm. pressure is 2 × 3·74 litres (approx.) = 7·48 litres (approx.).

(*c*) From the equation

$$3Fe + \underset{4 \times 18}{4H_2O} = Fe_3O_4 + \underset{4 \times 2}{4H_2}$$

we know that

4 × 18 grams of water will give rise to 4 × 2 grams of hydrogen, *i.e.*, 4 × 22·4 litres of hydrogen at N.T.P., since molecular weight of any gas expressed in grams occupy 22·4 litres at N.T.P. Therefore, 5·4 grams of water will produce $\frac{4 \times 22{\cdot}4}{4 \times 18} \times 5{\cdot}4$ or 6·72 litres of hydrogen at N.T.P., *i.e.*, the volume of hydrogen is the same as in case (*b*).

Therefore, the volume of hydrogen produced in this case at 27°C. and 750 mm. pressure is 7·48 litres (approx.).

Nascent hydrogen is the *new-born* hydrogen just produced from any of its compounds and as such it is obtainable at the moment of its liberation from its compounds. Its extra activity is oftentimes explained by supposing it to be in the *atomic state* under the condition stated above, not having had time enough to form a molecule by combining with another atom. There are also other explanations for its extra-activity, *viz.*, energy content of hydrogen in the nascent state, being high or the hydrogen liberated being under high pressure, the activity is exhibited.

Experiment to show that nascent hydrogen is a more powerful reducing agent than ordinary hydrogen :

A solution of potassium permanganate, $KMnO_4$ is prepared in water, diluted to sufficient extent. Next the solution is acidulated with dil. H_2SO_4. Hydrogen from a Kipp's apparatus is passed into a portion of this solution for about 15 to 20 minutes. The pink colour of the solution is *not* discharged. Next a few pieces of Zinc and dilute H_2SO_4 are added to the remaining portion of the same solution. The pink colour of the solution is discharged within a short time by the hydrogen evolved within the solution. This proves that the hydrogen in the nascent state is a more powerful reducing agent than ordinary molecular hydrogen.

$$2KMnO_4 + 3H_2SO_4 + 10H = K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Q. 2. **(Alternative)**. *Or, Give an account of the properties of carbon monoxide. How would you convert it into carbon dioxide and vice versa ?*

100 c.c. of a mixture of carbon monoxide, methane and hydrogen were mixed with 300 c.c. of oxygen and fired. After cooling, the resulting gases occupied 285 c.c. and after absorption by potash 205 c.c. of oxygen remained. Determine the composition of the mixture. All the gases were measured at the same temperature and pressure.

Ans. Properties of carbon monoxide, CO :

Carbon monoxide is a colourless gas with a peculiar faint smell. It is slightly lighter than air and is practically insoluble in water. The gas is extremely poisonous : it combines with the hæmoglobin of blood forming *carboxy-haemoglobin* which is incapable of absorbing oxygen ; thus blood in the lungs loses its capacity of taking up oxygen and thus brings about insensibility and ultimately death.

Carbon monoxide is a combustible gas. It burns with a characteristic lambent blue flame, forming CO_2, when ignited, $2CO + O_2 = 2CO_2$. An intimate mixture of carbon monoxide and oxygen when inflammed explodes violently.

It is a neutral oxide of carbon. It is an *unsaturated* compound and combines directly with chlorine, under the influence of sunlight, with the formation of carbonyl chloride, or *phosgene gas* : $CO + Cl_2 = COCl_2$. Finely divided nickel, cobalt and iron unite with carbon monoxide on heating, with the formation of a class of compounds called *carbonyls*, *e.g.*, nickel carbonyl, $Ni(CO)_4$, iron carbonyl, $Fe(CO)_5$ etc.

Carbon monoxide is a powerful reducing agent at an elevated temperature. Thus, when carbon monoxide is passed over red-hot copper oxide, CuO is reduced to metallic copper and CO is oxidised to CO_2. $CuO + CO = Cu + CO_2$. Solid KOH when heated absorbs CO when passed into it under pressure forming patassium formate ; $KOH + CO = HCOOK$. A solution of cuprous chloride in conc. HCl or in ammonia absorbs carbon monoxide, forming $CuCl, CO, 2H_2O$.

Conversion of carbon monoxide into carbon dioxide and vice versa :

When carbon monoxide is burnt in excess of air or oxygen, it is converted into carbon dioxide.

$$2CO + O_2 = 2CO_2.$$

Again when carbon dioxide is passed through a tube containing red-hot charcoal, it is converted into carbon monoxide.

$$CO_2 + C = 2CO.$$

Sum: —

Let x c.c. be the volume of carbon monoxide and y c.c. be the volume of methane present in 100 c.c. of the gas mixture. Then the volume of hydrogen present $= (100 - x - y)$ c.c.

Volume of carbon dioxide produced after explosion, as seen from KOH absorption $= (285 - 205)$ c.c.

$$= 80 \text{ c.c.}$$

Also the volume of oxygen used up in the explosion $= (300 - 205)$ c.c. $= 95$ c.c.

The reactions that take place can be represented by the following equations :—

$$\begin{array}{cccccc} 2CO & + & O_2 & = & 2CO_2 & \quad ...(1) \\ \text{2 vols.} & & \text{1 vol.} & & \text{2 vols.} & \end{array}$$

$$\underset{1\text{ vol.}}{CH_4} + \underset{2\text{ vols.}}{2O_2} = \underset{1\text{ vol.}}{CO_2} + 2H_2O \quad \ldots(2)$$

$$\underset{2\text{ vols.}}{2H_2} + \underset{1\text{ vol.}}{O_2} = 2H_2O \quad \ldots(3)$$

From equation (1) we know that

2 vols. of CO will require 1 vol. of oxygen for complete combustion and will give rise to 2 vols. of CO_2.

$\therefore$ x c.c. of CO will require $\frac{x}{2}$ c.c. of oxygen for complete combustion and will give rise to x c.c. of CO_2. Similarly, from equation (2), we know that

1 vol. of CH_4 will require 2 vols. of oxygen for complete combustion and will give rise to 1 vol. of CO_2.

$\therefore$ y c.c. of CH_4 will require $2y$ c.c. of oxygen for complete combustion and will give rise to y c.c. of CO_2. From equation (3), we know that

2 vols. of hydrogen will require 1 vol. of oxygen for complete combustion.

$\therefore$ $(100 - x - y)$ c.c. of hydrogen will require $\frac{100 - x - y}{2}$ c.c. of oxygen for complete combustion.

Hence, from the data given, and from the suppositions made, we have

$$x + y = 80 \ldots\ldots(1)$$

$$\frac{x}{2} + 2y + \frac{100 - x - y}{2} = 95 \ldots\ldots(2)$$

From (2), we have $\frac{3y}{2} = 95 - 50 = 45$

$$\therefore \quad 3y = 90$$
$$\therefore \quad y = 30 \text{ c.c.}$$
$$\therefore \quad x = 50 \text{ c.c. from (1).}$$

Thus CO present $= 50$ c.c.
CH_4 present $= 30$ c.c.
and H_2 present $= (100 - 50 - 30)$ c.c.
$= 20$ c.c.

Q. 3. *What is meant by* **hard** *and* **soft** *water? What causes hardness of water and why?*

State, giving reasons for your answer, to which of these tw categories each of the following samples of water belongs : (a) rain water, (b) sea water, (c) water derived from clear ice produced by partially freezing sea water.

What are the disadvantages of hard water ? Describe methods by which you could remove hardness of water.

Ans. Hard water is that kind of water which does not easily produce lather with soap, but does so after much soap is consumed. Soft water easily produces lather with soap and so practically no soap is wasted.

Hardness of water is due to the presence of soluble calcium and magnesium salts in solution. When the hardness is due to the presence of bicarbonates of calcium and magnesium in solution, it is called 'temporary hardness' ; but when the hardness is due to the presence of chlorides and sulphates of calcium and magnesium in solution, it is called 'permanent hardness' of water. When soluble salts of calcium and magnesium are present in water, double decomposition takes place with the constituents of soap which contains soluble sodium and potassium salts of organic acids like palmitic acid, stearic acid, etc., and calcium and magnesium salts of those organic acids are precipitated. These insoluble compounds of calcium and magnesium form a scum on the surface of water when hard water is treated with soap and no soap is available for cleansing purpose till all the calcium and magnesium salts are removed by precipitation. Thus much soap is wasted.

(*a*) Rain water belongs to the category of soft water. This is because of the faet that it is nothing but a kind of naturally distilled water and therefore contains no dissolved calcium or magnesium salts.

(*b*) Sea water belongs to the category of hard water. This is because of the fact that along with sodium chloride, it contains soluble calcium and magnesium salts, especially chlorides and sulphates, washed down by rivers into the seas. Sea water contains 3·6% of total solids by weight of which 2·6% is sodium chloride and the rest other salts.

(*c*) Water, derived from clear ice produced by partially freezing sea water, belongs to the category of soft water. Although sea water is hard as stated in (*b*), when it is partially frozen, pure water is converted into ice first : water derived by melting that ice, therefore, contains practically no dissolved salt and hence it are soft.

The *disadvantages* of hard water are :

(1) Hardness of water makes its unsuitable for washing purpose for the reasons stated above, as much soap and sodium carbonate are consumed.

(2) Hard water cannot be used in boilers as boilerfeed water. This is because by evaporation of such water calcium and magnesium salts are deposited on the inner surfaces of the boilers producing what are known as boiler-scales and 'furs' ; thereby much fuel is wasted to heat the water used in boilers and the deposit also damages the boiler-plates. Not only the use of hard water suffers from the disadvantage mentioned, but also, when $MgCl_2$ is present in hard water, HCl is evolved during boiling of such water and corrodes the boiler-plates.

$$MgCl_2 + H_2O = MgO + 2HCl.$$

(3) Hardness of water makes it unsuitable for use in the laboratory for purposes which require the use of distilled water, *viz.*, development of photographic plates, chemical analysis, etc.

Methods for removing hardness of water.

(*a*) Temporary hardness can be removed *by boiling* when the soluble bi-carbonates of calcium and magnesium are converted into soluble calcium or magnesium carbonates. On keeping, these settle down at the bottom of the vessel in which the water is boiled and the sample of water taken off from the top is soft.

$$\underset{\text{(Sol.)}}{CaH_2(CO_3)_2} = \underset{\text{(insol.)}}{CaCO_3} + H_2O + CO_2$$

$$\underset{\text{(Sol.)}}{MgH_2(CO_3)_2} = \underset{\text{(insol.)}}{MgCO_3} + H_2O + CO_2.$$

Temporary hardness can also be removed by Clark's process. In this process the requisite amount of lime in the form of lime-water or milk-of-lime is added to the temporarily hard water when soluble bi-carbonate of Ca and Mg are converted into insoluble carbonates.

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

In the case of the hardness being due to magnesium bicarbonate, twice the quantity of lime must be added, since magnesium carbonate is soluble in water to a certain extent, whilst the hydroxide of magnesium is much less soluble.

$$MgH_2(CO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O.$$

Permanent hardness cannot be removed either by boiling or by Clark's process. This kind of hardness is removed by the addition of sodium carbonate (washing soda) when the soluble sulphates and chlorides of Ca and Mg present in permanently hard water are converted into the insoluble carbonates of Ca and Mg.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$
$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4.$$

The modern Permutit Process.—The most modern method for the removal of hardness, both temporary and permanent, is known as Gan's Permutit Process. In this process, bodies, called permutits, which are mixtures of aluminium silicate, sodium silicate, etc., are employed. These silicate mixtures are called permutits because these have the capacity of exchanging bases.

The method depends upon the fact that if hard water be filtered through a bed of permutit, the sodium salt present in it will react with soluble calcium and magnesium salts present in hard water, producing insoluble calcium and magnesium permutit and the filtrate, being altogether free from Ca and Mg-salts, is soft.

Sodium permutit + Ca-salt = Calcium permutit + Na-salt. When the permutit bed, due to long use, is exhausted, it is reactivated by stopping the flow of hard water and passing a solution of common salt, NaCl, over the bed, when Na-permutit is regenerated according to the equation,

$$\text{Ca-permutit} + NaCl \rightarrow \text{Na-permutit} + CaCl_2$$
$$\text{Mg-permutit} + NaCl \rightarrow \text{Na-permutit} + MgCl_2.$$

Thus permutit can be regenerated and used over and over again.

Q. 4. *Describe how fluorine was isolated and give a neat outline of the apparatus used. Describe its properties and compare them with those of chlorine.*

Why was it not found possible to isolate fluorine by a method similar to that employed for chlorine ?

Ans. Preparations of Fluorine by Moissan's method.—Flourine is prepared by the electrolysis of a solution of potassium hydrogen fluoride, KF, HF, in anhydrous hydro-fluoric acid, HF. The apparatus consists of a *U*-tube made of an alloy of Platinum-Iridum provided with two side-tubes and is fitted with fluorspar stoppers. Two electrodes made also of Platinum-Iridium alloy and thickened at the bottom pass through these fluorspar stoppers. The whole apparatus is kept immersed in a bath of boiling methyl chloride at about $-23°C$. The *U*-tube is $\frac{2}{3}$rd filled up with the electrolyte, a solution of KF, HF in anhydrous HF. On passing the current through the eletrolyte HF undergoes decomposition, H_2 being liberated at the cathode and Fluorine at the anode. The Fluorine is led through a spiral of Pt kept immersed in boiling methyl chloride to remove any HF vapour by condensation. The gas is next passed through a tube of Pt packed with NaF which removes the last trace of HF. Fluorine is collected in a Pt-vessel by the upward displacement of air.

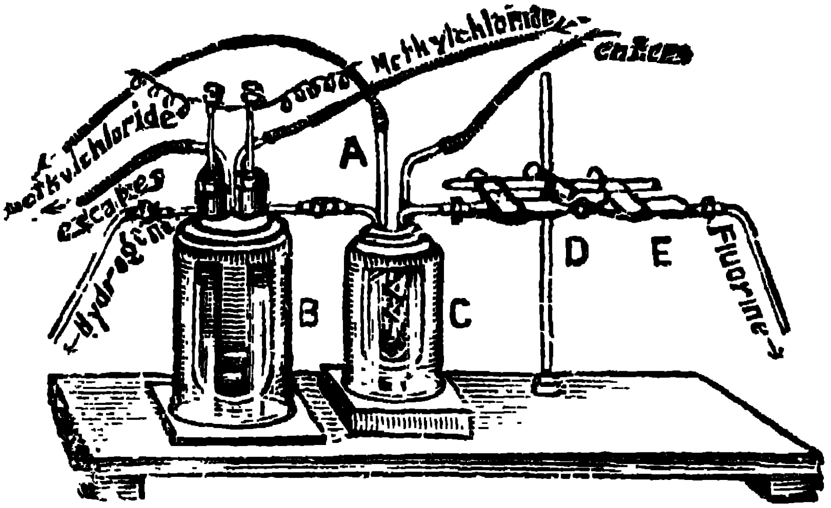


Fig. 1

Comparison of Fluorine, Chlorine, Bromine and Iodine.—(Points of comparison between F_2 and Cl_2 can be gathered from the general comparison of halogens given.) The physical properties of these elements exhibit a regular gradation with increasing atomic weight. Thus Fluorine and Chlorine are gasses, Bromine is liquid, while Iodine is solid at ordinary temperatures. Fluorine is faintly greenish-yellow in colour, Chlorine is greenish-yellow, Bromine vapour is brownish-red and Iodine vapour is violet. Thus the colour deepens with increasing atomic weight. About solubility of these elements in water Fluorine decomposes water and so its solubility is not known, Chlorine is fairly soluble, the solubility of Bromine is greater than that of Chlorine whereas Iodine is very slightly soluble.

In their chemical activity they also show the same gradual change ; thus, in the case of their combination with Hydrogen, when Fluorine and Hydrogen are brought together, combination instantly takes place with explosion, even in the dark. Chlorine and Hydrogen do not combine in the dark, but in diffused daylight they combine slowly, and in direct sunlight the combination takes place suddenly with explosion. Bromine vapour and Hydrogen do not combine even in direct sunlight, a mixture of the two gases combines when heated, yielding HBr, while Iodine vapour and Hydrogen require to be strongly heated in contact with spongy Pt to effect their combination. Fluorine decomposes water at the ordinary temp., giving off ozonised Oxygen, whereas Chlorine decomposes water when Cl_2—water is kept exposed to sunlight, Bromine slowly decomposes water when Br_2—water is kept exposed to sunlight and Iodine has no action on water. About bleaching properties, Fluorine decomposes the vegetable colouring matter. Chlorine readily bleaches, Bromine bleaches slowly whereas Iodine has very slight bleaching properties. About their chemical activities, Fluorine is the most active of them all and can liberate Cl_2, Br_2 and I_2 from Chlorides, Bromides and Iodides ; Chlorine is less active than Fluorine and can liberate Br_2 and I_2 from Bromides and Iodides ; Bromine is less active than Chlorine and can liberate only Iodine from Iodides, whereas Iodine is the least active of them all. One definite oxide, F_2O is known in the case of Fluorine, Chlorine forms several unstable oxides by indirect combination, unstable oxides are known in the case of Bromine whereas several stable oxides are known in the case of Iodine. Here the gradation is not very marked. Reactions of these elements with starch solution is characteristic : Fluorine attacks water of the starch solution, Chlorine has no action, Bromine colours the starch solution yellow and Iodine gives a blue coloration with starch solution.

Although a strong resemblance exists between all the members of the halogen family, the element Fluorine, which is the *typical* member, stands marked off from the others in many of its attributes. Thus Fluorine exhibits a great tendency to form double salts which have no counterpart among the compounds of the other elements of the family, and at temperatures below 32°C. the molecule of hydro-fluoric acid consists of two atoms of hydrogen and two of fluorine, having the composition H_2F_2. Among the compounds of Fluorine also this difference in behaviour is very marked. Thus, Silver fluoride is soluble in water, whereas Silver chloride, bromide and iodide are all insoluble. Calcium fluoride is insoluble in water where as other Calcium halides are extremely soluble in water.

Properties of Fluorine.—Fluorine is a pale greenish-yellow gas, paler and more yellow in colour than Chlorine. It has a characteristic irritating smell, and attacks the mucous membranes of nose and throat. It is heavier than air.

Its affinity for hydrogen is greater than that of chlorine. The two gases combine even in the dark at the ordinary temperature (or even at low temperatures) with explosive violence, $H_2 + F_2 = 2HF$. It also combines with hydrogen present in other hydrogen compounds. When passed into water, fluorine immediately reacts with hydrogen of water forming HF and liberating a mixture of oxygen and ozone.

$$2F_2 + 2H_2O = 4HF + O_2$$
$$3F_2 + 3H_2O = 6HF + O_3.$$

Fluorine reacts with nearly all elements with the exception of Nitrogen, Helium, Argon, etc. Fluorine is the most active of all the halogens, and as such is capable of liberating Cl_2, Br_2 and I_2 from their respective compounds :

$$2KCl + F_2 = 2KF + Cl_2.$$

Sulphur, iodine, bromine, arsenic, crystalline silicon, boron and powdered charcoal become incandescent when brought into contact with Fluorine and combine with it. Sodium, potassium, calcium, etc., take fire in the gas spontaneously. Magnesium, aluminium, silver, etc., required warming for the reaction to set in and then take fire and burn in the gas. Lead is slowly attacked at the ordinary temperature and copper becomes coated with a protective layer of fluoride when brought in contact with Fluorine.

Fluorine reacts with 2% NaOH solution forming fluorine monoxide :

$$2NaOH + 2F_2 = 2NaF + F_2O + H_2O.$$

Fluorine cannot be isolated by a method similar to that employed for Chlorine, *viz.*, oxidation of its hydracid, HCl, either by MnO_2 or by other oxidising agents or by electrolysis of HCl or of fused chlorides or solution of soluble chlorides, for the following reasons :—

(1) Fluorine is the most active electro-negative element and combine with all metals and almost all non-metals. Therefore, even though oxidation by oxidising agents of hydrogen fluoride might liberate Fluorine, that Fluorine will attack the elements of the oxidising agents, Mn etc., and combine with them.

(2) Moreover, Fluorine has the most strong affinity for hydrogen and as such splitting up of HF into its elements during oxidation is not possible. Even though such splitting be assumed,—water, formed by oxidation of hydrogen, will at once be attacked by liberated Fluorine and HF will be produced.

(3) For the same reasoning as in (1), the electrolysis of metallic fluorides cannot yield free Fluorine.

(4) Anhydrous HF is a non-conductor of electricity. Aqueous HF, when electrolysed, yields hydrogen at the cathode and oxygen at the anode. So no Fluorine can be obtained by this method.

No suitable vessel can be found easily for the preparation of Fluorine by the methods used for getting chlorine.

Q. 5. *How would you determine the volumetric composition of ammonia and deduce its formula therefrom ?*

Describe the action of ammonia gas on (a) heated sodium, (b) solution of mercuric chloride, (c) precipitated silver chloride suspended in water. Give equations.

Ans. The composition of ammonia is determined by Hoffmann's method.

The fact that ammonia is decomposed by chlorine producing N_2 and forming NH_4Cl is taken advantage of in this method to show the volumetric composition of Ammonia.

A long glass tube fitted with a stop-cock at one end and a small dropping funnel at the other, is marked off into three equal divisions by India-rubber rings (Fig. 2). The tube is completely

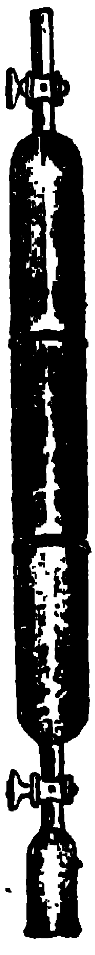


Fig. 2.

filled up with chlorine gas. A strong solution of ammonia is admitted into the tube drop by drop from the funnel until the reaction between the chlorine and ammonia ceases. Chlorine combines with the hydrogen of ammonia giving HCl and nitrogen is set free. HCl now reacts with excess of ammonia producing white fumes of NH_4Cl.

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

When an excess of ammonia has been added to ensure its complete conversion into NH_4Cl and N_2, the excess of ammonia is neutralised by adding dilute H_2SO_4 in excess. The stop-cock of the dropping-funnel is now turned off, and the tube is placed in a tall jar containing water. The bottom stop-cock is now opened, when water rushes up and fills the tube nearly upto the second mark from the bottom. The level of water inside and outside the tube is now made the same, when the residual gas is found to occupy one-third of the vol. of chlorine taken. That the residual gas in nitrogen is proved by the facts that it is inert, does not readily combine with other elements and it is absorbed by strongly heated Magnesium.

We know that Hydrogen and Chlorine combine in equal volumes to form HCl gas. Therefore, 3 vols. of Chlorine taken in the tube, must have combined with 3 vols. of Hydrogen. These 3 vols. of Hydrogen must have come from Ammonia gas, which has simultenaeously liberated 1 vol. of Nitrogen. Thus, *ammonia is made up of one volume of Nitrogen combined with three volumes of Hydrogen.*

Let 1 vol. of Nitrogen contain "n" number of molecules $\therefore$ "n" molecules of Nitrogen combine with "$3n$" molecules of Hydrogen to form Ammonia (Avogadro) or 1 molecule of Nitrogen combines with 3 molecules of Hydrogen to form Ammonia.

But both Nitrogen and Hydrogen molecules are diatomic, $\therefore$ 2 atoms of Nitrogen combine with 6 atoms of Hydrogen to give Ammonia.

$$\text{or, } \frac{\textit{No. of atoms of Nitrogen present in Ammonia}}{\textit{No. of atoms of Hydrogen present in Ammonia}} = \frac{2}{6} = \frac{1}{3}.$$

Hence the formula for Ammonia is $(NH_3)x$. Now the density of Ammonia determined experimentally is 8·5. $\therefore$ the molecular wt. of Ammonia is 17. This tallies with the formula NH_3. Hence the molecular formula for Ammonia is NH_3, x being equal to 1.

(*a*) When Ammonia gas is passed over heated metallic sodium, sodamide is formed and Hydrogen is liberated :

$$2Na + 2NH_3 = \underset{\text{Sodamide.}}{2NaNH_2} + H_2$$

(*b*) When Ammonia gas is passed into a solution of mercuric chloride, a white precipitate of amido-mercuric chloride, NH_2HgCl is formed and hydrochloric acid is produced in solution. The white pecipitate is known as infusible white precipitate.

$$HgCl_2 + NH_3 = \underset{\text{infusible white ppt.}}{NH_2HgCl} + HCl$$

(*c*) On passing Ammonia gas through silver chloride suspended in water, silver chloride passes into solution forming silver ammine chloride, $Ag(NH_3)_2Cl$.

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl.$$

Q. 6. *Explain and illustrate each of the following :—*

(*a*) *Catalytic agent*, (*b*) *Oxidation and reduction*, (*c*) *chemical changes by silent electric discharge.*

Ans. (*a*) *Catalytic agent.*—When a substance, by its mere presence, in small quantities, influences the rate of a chemical reaction, without itself undergoing any change in mass and in chemical composition, it is called a catalytic agent.

Thus, in the preparation of oxygen from $KClO_3$, MnO_2 is added to hasten the rate of decomposition of $KClO_3$ by heat, Here, MnO_2 acts as a catalytic agent, because it does not undergo any alteration in mass or in chemical composition during the reaction as shown by experiments after the decomposition of $KClO_3$ is complete by dissolving out the KCl formed by water.

(*b*) **Oxidation** implies addition of oxygen or any electro-negative element to an element or a compound, as also removal of hydrogen or any electro-positive element from a compound.

Reduction implies the reverse operation of oxidation ; thus addition of hydrogen or of any electro-positive element to an element or a compound as also the removal of oxygen or of any electro-negative element from a compound, are termed reduction.

Thus, when sulphur is burnt in oxygen, it combines with oxygen, giving sulphur dioxide and so sulphur is oxidised.

$$S + O_2 = SO_2.$$

When iron is heated in a stream of chlorine gas, it combines with chlorine giving ferric chloride ; thus iron is oxidised.

$$2Fe + 3Cl_2 = 2FeCl_3.$$

When hydrochloric acid is heated with manganese dioxide, it gives rise to chlorine gas by loss of hydrogen ; so hydrochloric acid is oxidised :

$$4\,HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

When potassium iodide is treated with hydrogen peroxide, iodine is liberated ; thus potassium iodide is oxidised to iodine by loss of potassium, an electro-positive element :

$$2\,KI + H_2O_2 = 2\,KOH + I_2.$$

Similarly, when hydrogen gas is passed over heated copper oxide, it is reduced to metallic copper (removal of oxygen) :

$$CuO + H_2 = Cu + H_2O,$$

When sulphuretted hydrogen is passed into iodine suspended in water, iodine is reduced to hydriodic acid (addition of hydrogen) :

$$H_2S + I_2 = 2HI + S.$$

When ferric chloride solution is treated with zinc and hydrochloric acid, it is converted into ferrous chloride (loss of an electro-negative element chlorine) by reduction with nascent hydrogen :

$$FeCl_3 + H = FeCl_2 + HCl$$

When metallic sodium is heated in a current of chlorine, sodium chloride is formed by reduction of chlorine (addition of an electro-positive element) :

$$2Na + Cl_2 = 2NaCl.$$

Among inorganic compounds, oxidation usually denotes an increase in the positive valency of an element, *e.g.* when ferrous chloride is oxidised to ferric chloride, the valency of iron increases from $+2$ to $+3$; when stannous chloride is oxidised to stannic chloride, the valency of tin increases from $+2$ to $+4$.

From ionic standpoint, if we take into consideration the reaction

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2,$$

it can be represented as

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised by the loss of two electrons which have passed to the ferric ions, reducing them to the ferrous state.

Hence; oxidation may be defined as the operation in which there is loss of electron and reduction as the operation in which there is gain in electron.

Moreover, it must also be observed that oxidation and reduction take place simultaneously. Whenever a substance is oxidised, another one is reduced. Thus when stannous chloride solution is added to a solution of mercuric chloride, a white precipitate of mercurous chloride is produced. Here mercuric chloride is reduced to mercurous chloride, but at the sametime stannous chloride is oxidised to stannic chloride.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

(*c*) When the terminals of an induction coil are connected with two metallic conducting surfaces, separated by a suitable distance, and the induction coil is worked, a silent electric discharge occurs, without the appearance of any spark. This silent electric discharge has the property of bringing about certain chemical changes in substances placed in its sphere of action.

For example, ozone mixed with oxygen is obtained by passing *dry oxygen* through the annular space of two coaxial glass tubes, the inner surface of the inner tube and the outer surface of the outer tube being lined with tin-foils, which in their turn are connected with the terminals of an induction coil in operation when a silent electric discharge passes through the annular space. Chemical change occurs and conversion of dry oxygen into ozone takes place.

$$3O_2 = 2O_3.$$

Q. 7. *How could you obtain :*

(*a*) *Sulphur and hydrogen from sulphuretted hydrogen ;*

(*b*) *Lead, nitrogen and oxygen from lead nitrate ;*

(*c*) *Potassium, chlorine and oxygen from potassium chlorate ?*

Ans. When sulphuretted hydrogen taken in a closed tube is subjected to the action of electric sparks, it is decomposed into hydrogen and suphur. Sulphur is deposited in the solid state and hydrogen gas remains in the tube and so the two elements present in sulphuretted hydrogen can be obtained separately.

$$H_2S = H_2 + S.$$

Again, when sulphuretted hydrogen is passed into bromine-water, sulphur is deposited in the solid state. The solution is boiled and filtered when sulphur remains on the filter-paper. Thus, sulphur can be obtained from sulphuretted hydrogen.

$$H_2S + Br_2 = 2HBr + S.$$

Also, by heating a piece of metallic tin in sulphuretted hydrogen, hydrogen can be obtained as a gaseous residue.

$$H_2S + Sn = SnS + H_2.$$

(*b*) Powdered lead nitrate is to be taken in a hard glass test-tube fitted with a cork through which passes a delivery tube. The delivery tube is connected to one limb of a *U*-tube immersed in freezing mixture. The other limb of the *U*-tube is connected with a delivery tube dipped under water in a pneumatic trough (not shown in the figure), over which a gas-jar full of water is inverted.

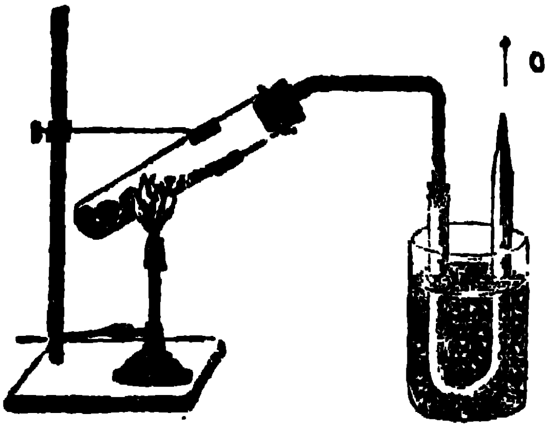


Fig. 3

The hard glass test-tube containing lead nitrate is next heated when lead nitrate decomposes into lead oxide (left as a yellow residue in the test-tube), nitrogen peroxide (which collects as a yellow liquid in the *U*-tube kept immersed in freezing mixture), and oxygen (which collects in the gas-jar by displacement of water).

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The gas collected in the gas-jar rekindles a glowing chip of wood, produces brown fumes with nitric oxide and is completely absorbed by alkaline pyrogallate. Thus, the gas is proved to be nothing but oxygen.

Next, the liquid nitrogen peroxide is taken out from the *U*-tube and is vapourised by heating and the gas is passed through a hard glass tube packed with copper turnings heated to redness. The issuing gas from the hot tube is collected by suitable arrangement in a gas-jar by displacement of water. The gas is found to be inert, a non-supporter of combustion, incapable of turning lime-water milky and to be absorbed by heated magnesium. This proves the gas to be nitrogen.

$$2NO_2 + 4Cu = 4CuO + N_2.$$

The yellow residue left in the hard glass test-tube is then taken out, mixed with sodium carbonate, taken on a charcoal groove and heated in the reducing blow-pipe flame. A bright malleable metallic bead is obtained. The bead marks paper. This bead is then dissolved in nitric acid, the acid is neutralised and potassium chromate solution is added, when a yellow precipitate is formed, proving the bead to be of lead.

$$PbO + 2C = Pb + 2CO\ ;$$
$$Pb + 4HNO_3 = Pb(NO_3)_2 + 2H_2O + 2NO_2.$$
$$Pb(NO_3)_2 + K_2CrO_4 = \underset{\text{Yellow ppt.}}{PbCrO_4} + 2KNO_3.$$

(*c*) Potassium chlorate is taken in a hard glass test-tube fitted with a cork and a delivery tube. The delivery tube is dipped under water in a pneumatic trough, over which a gas-jar full of water is inverted. The hard glass test-tube is next heated when a gas is evolved and is collected in the gas-jar by displacement of water. A white solid residue is left in the test-tube.

$$2KClO_3 = 2KCl + 3O_2.$$

The gas collected in the gas-jar is found to be capable of rekindling a glowing chip of wood, of producing brown fumes with nitric oxide and to be absorbed completely by alkaline pyrogallate, proving it to be nothing but oxygen.

The residue in the hard glass test-tube is divided into two portions.

(*i*) One part is mixed with MnO_2 and concentrated sulphuric acid and heated in a flask provided with a cork and a delivery tube. The greenish-yellow gas evolved is collected by upward displacement of air.

$$2KCl + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + Cl_2 + 2H_2O.$$

That the gas is chlorine is proved by its greenish-yellow colour, pungent odour like that of bleaching powder and its capacity to turn starch-iodide paper blue.

(*ii*) The other part of potassium chloride is first purified by recrystallisation and then fused in an iron vessel and is electrolysed as in Down's process for extraction of sodium. Potassium is liberated at the cathode and chlorine gas at the anode. Potassium is protected from the action of chlorine and is collected as usual.

That the metal collecting is potassium is proved by determining its sp. gr. (0·86), its melting point (62°C.) and its property of imparting a violet colour to the non-luminous Bunsen flame (the flame appearing red when viewed through double-blue glass) when it is treated with HCl and held in a Pt. wire in the non-luminous flame.

Q. 8. *Name the important ores of copper. Describe the method of extracting copper from its sulphide ores giving equations for the reactions that occur. How is the crude metal refined ?*

Name two important alloys of the metal with their constituents. State the uses of the metal and the alloys.

Ans. *The important ores of copper are :*

(1) Ruby ore, red copper ore or cuprite, Cu_2O.

(2) Copper glance, Cu_2S.

(3) Covellite or indigo copper, CuS.

(4) Copper pyrites, Cu_2S, Fe_2S_3 or $CuFeS_2$.

(5) Purple copper ore, $3Cu_2S$, Fe_2S_3 or Cu_3FeS_3.

(6) Malachite, $CuCO_3$, $Cu(OH)_2$.

(7) Azurite, $2CuCO_3$, $Cu(OH)_2$.

Extraction of copper from its sulphide ores :—Copper pyrites is generally used for extraction of copper by a Thermal process.

At first the ore is concentrated either by gravity separation or by Floatation process. For this purpose the ore is first crushed and finely powdered. The powdered ore is next churned with water containing a little pine oil and lime, by blowing air through it. By this operation a froth is produced, which carries up along with it the particles of copper ore, it being preferentially wetted by oil ; sand and other impurities are left in the bottom of the vessel, these being preferentially wetted by water. The froth is collected by skimming and allowed to settle.

The concentrated ore is next roasted in a multiple hearth furnace, whereby sulphur present in the ore is partially burnt out, forming SO_2 and the metals are partially oxidised.

$$Cu_2S.Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S.Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$

This last reaction occurs only to a very small extent. The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when a little quantity of Cu_2O formed in the previous operation reacts with iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO,$$

The ferrous oxide so formed and also produced in the previous operation reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained of cuprous and ferrous sulphides is known as *matte.* The molten matte is then directly run into a Bessemer converter with a little silica and a blast of air is introduced through tuyeres placed at the sides. Iron is first oxidised to FeO which combines with silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued. Cu_2S is then partially oxidised to Cu_2O and this Cu_2O reacts with unchanged Cu_2S to form copper and SO_2. The slag is removed, the blast stopped and the converter tilted to pour off Cu. This copper has a blistered appearance due to escape of SO_2.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

Thermal Refining :—

Blistered copper is then melted on the hearth of a reverberatory furnace when the impurities are oxidised. Some escape as gas, others form slag with the furnace lining of silica, which is removed. Next the metal begins to oxidise. Anthracite coal is then sprinkled on the molten mass and the mass is stirred with logs of green wood. When the copper attains the requisite *tough-pitch*, it is poured out.

Electrolytic refining of commercial metal :—

Thick sheets of impure metallic copper are suspended from a metal rod which is the anode in a bath of $CuSO_4$ solution *acidified* with dil. H_2SO_4 taken in an wooden vessel lined with lead. Thin plates of pure copper are suspended from another metal rod which is made the cathode and are inserted alternately between the thick sheets. A little HCl is added to the bath to precipitate out any silver present in the impure copper sheets. On passing electric current through the bath of copper sulphate, the thick sheets gradually pass into solution and pure copper is deposited on thin plates. Impurities either pass into solution or are deposited at the bottom of the bath. Copper, thus obtained at the cathode, is 99·99 per cent pure.

The **two** important alloys of copper are.

(*1*) Brass, an alloy of copper and zinc and (*2*) Bronze, an alloy of copper and tin.

Uses of copper—Copper is used largly in electric industry, in electrotyping, for cables and wires conveying electric current ; in the preparation of household untensils, for coinage and for the preparation of alloys, like brass, bronze, german silver, etc. Brass is used for preparing household utensils. Bronze is used in coinage and for making medals, statues, etc.

SECOND PAPER—1941

Q. 1. *40 c.c. of oxygen measured at N.T.P. were contained in a tube of cross-section of 1·2 sq. cm. The upper end of the tube was sealed and it stood on a trough of mercury, the level of mercury inside the tube being at a height of 15·6 cm. The temperature of the room was 31°C. and the atmospheric pressure was 756 mm. of mercury. Calculate the length of the gas inside the tube.*

Ans. Let V c.c. be the volume of the quantity of oxygen under the conditions existing inside the tube. Now 15·6 cm. = 156 mm. and therefore the pressure to which the oxygen is subjected is (756 − 156) mm. = 600 mm. The temperature of the oxygen present in the tube = (273 + 31)° Absolute = 304° Absolute.

Then by Boyles' and Charles' laws, we have

$$\frac{40 \times 760}{273} = \frac{V \times 600}{273 + 31},$$

$$\text{whence,} \quad V = \frac{40 \times 760 \times 304}{600 \times 273} \text{ c.c.} = 56{\cdot}42 \text{ c.c.}$$

But the cross-section of the tube was 1·2 sq. cm. Let l cm. be the length of the tube occupied by this volume of oxygen.

Then $1{\cdot}2 \times l = 56{\cdot}42$,

whence $l = \frac{56{\cdot}42}{1{\cdot}2}$ cm. $= 47{\cdot}02$ cm. (approx.)

Q. 2. *Explain the meaning of the terms 'equivalent weight' and 'atomic weight'. How are they related to each other?*

Describe a method for the determination of the equivalent weight of copper or potassium.

Equivalent weight of an element is that weight of it which can combine with or displace 1 part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine,, etc. Thus, equivalent weight of an element

$$= \frac{\text{Weight of the element}}{\text{Weight of hydrogen, combined}}$$

with or displaced by the weight of the element taken.

Thus the equivalent weight is a mere number. *Gram-equivalent* of an element is its equivalent weight expressed in grams. It is known from experiment that 35·5 grams of chlorine combine with one gram of hydrogen. Therefore 35·5 is the equivalent weight of chlorine.

The atomic weight of an element expresses how many times an atom of an element is heavier than an atom of hydrogen. Thus,

Atomic weight of an element

$$= \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of hydrogen}}.$$

Hence it is also a mere number. *Gram-atom* of an element is the atomic weight of the element expressed in grams.

Also the atomic weight of an element is the smallest weight of it ever found in the molecular weights of its compounds.

Thus, 14 is the atomic weight of nitrogen, and all compounds of nitrogen, in their molecules, contain at least 14 parts by weight of nitrogen, or some multiples of 14 parts by weight of nitrogen. Also atom of nitrogen is 14 times heavier than an atom of hydrogen, Now, the relationship between equivalent weight and atomic weight of an element is expressed as : Equivalent weight × valency = Atomic weight.

The *equivalent weight of copper* is determined by the following experiment :

A porcelain crucible with its lid is taken. It is thoroughly cleansed, dried, heated on a clay-pipe triangle for about half an hour, cooled in a desiccator and weighed in a chemical balance. Heating, cooling and weighing is continued till the weight of the crucible with lid becomes *constant*. Next a little amount of pure copper wire is taken in the crucible and after placing the lid in position, the crucible with its contents is weighed again in the chemical balance. The difference in the two weighings will give the weight of copper taken. Now the crucible is placed on an asbestos board, the lid is pushed aside a little and conc. nitric acid is added to copper wire drop by drop till the metal is completely dissolved. The crucible is to be kept nearly covered during the reaction. The crucible is next placed on a water-bath after pushing the lid aside and the solution is evaporated slowly, taking care that there is no loss of solution by spurting. The green residue left in the crucible is of copper nitrate. Next the crucible is strongly heated over a Bunsen flame by placing it on a clay-pipe triangle with the lid pushed aside a little at first and then covered completely till the copper nitrate is completely converted into black copper oxide. The crucible with the lid is then cooled in a desiccator and weighed again. The process of heating, cooling in a desiccator and weighing is continued till the final weight is constant.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

Calculations :—

Let the weight of the crucible and lid $= w_1$ grams.
The weight of the crucible and lid + copper $= w_2$ grams.
∴ Wt. of copper taken $= (w_2 - w_1)$ grams.

Last weight of the crucible and lid + copper oxide $= w_3$ grams.

∴ Wt. of oxygen combined with the given weight of copper $= (w_3 - w_2)$ grams. Thus $(w_3 - w_2)$ grams of oxygen has combined with $(w_2 - w_1)$ grams of copper to form copper oxide.

Therefore 8 grams of oxygen will combine with

$$\frac{w_2 - w_1}{w_3 - w_2} \times 8 \text{ grams of copper.}$$

Hence, by definition, the equivalent weight of copper

$$= \frac{w_2 - w_1}{w_3 - w_2} \times 8.$$

Equivalent weight of Potassium:

A weighed quantity of pure re-crystallised potassium chloride is taken in a beaker and is than dissolved completely in distilled water. The solution is next made *slightly acidic* with dilute nitric acid. Then silver nitrate solution is slowly added with constant stirring until the precipitated silver chloride coagulates and settles at the bottom. A few drops more of silver nitrate solution is then added to see that the precipitation is complete and no more turbidity appears where the two solutions meet.

$$KCl + AgNO_3 = AgCl + KNO_3.$$

The liquid is then heated and filtered through a Gooch crucible, previously prepared and weighed to a constant weight. The precipitate is thoroughly washed with distilled water to free it from adhering silver nitrate and potassium nitrate. Then the Gooch crucible is dried in an air-oven, cooled in a desiccator and weighed. Heating in an air-oven, cooling in a desiccator and weighing is continued till the final weight is constant. The difference between the two weighings of the Gooch crucible will give the weight of AgCl produced from a known weight of KCl.

Calculation :

Let the weight of KCl taken $= w_1$ gms.
and the weight of AgCl formed $= w_2$ gms.

Now, in $(108 + 35{\cdot}5)$ or $143{\cdot}5$ parts by weight of AgCl, there are $35{\cdot}5$ parts by weight of chlorine.

$\therefore$ in w_2 gms. of AgCl, we have $\frac{w_2 \times 35{\cdot}5}{143{\cdot}5}$ gms. of chlorine.

And this amount of chlorine has come from w_1 gms. of KCl. Hence the weight of K present in w_1 gms. of KCl $= w_1 - \frac{w_2 \times 35{\cdot}5}{143{\cdot}6} = w_3$ gms., say.

Then, $\frac{w_2 \times 35{\cdot}5}{143{\cdot}6}$ gms. of chlorine has combined with w_3 gms. of K.

$\therefore$ 35·5 gms. of chlorine can combine with

$$\frac{w_3}{\frac{w_2 \times 35{\cdot}5}{143{\cdot}5}} \times 35{\cdot}5 \text{ gms.} = \frac{w_3 \times 143{\cdot}5}{w_2} \text{ gms. of K.}$$

Hence, by definition, the equivalent weight of potassium

$$w_3 \times 143{\cdot}5$$

Q. 3. *A few grams of potassium got mixed up with mercury. The mixture was treated with water and the aqueous solution was then separated, warmed and allowed to be mixed up with a stream of chlorine gas. When the solution was almost saturated with chlorine, a crystalline product, seperated out. This was filtered, dried and kept at about 300°C. for some time. This was then crystallised from the hot water. What is the final product ?*

Indicate with equations the different changes that had taken place.

Ans. (*a*) When the potassium got mixed up with mercury, potassium amalgam was produced. This potassium amalgam may be a compound of potassium and mercury of the composition KHg_2, or simply it may be a solution of potassium in mercury.

(*b*) When this potassium amalgam was treated with water, potassium reacted with water producing hydrogen and caustic potash, and mercury was set free.

$$2K + 2H_2O = 2KOH + H_2.$$

(*c*) The aqueous solution containing this caustic potash, when warmed and nearly saturated with chlorine, gave the crystalline product potassium chlorate, $KClO_3$ and potassium chloride, KCl, also formed simultaneously, remained in solution.

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

(*d*) When the crystals were collected and dried and kept at about 300°C. for some time, no change occured and potassium chlorate remained in tact. (Potassium chlorate fuses at 357°C. and begins to decompose at 372°C. Under these conditions potassium perchlorate is formed along with potassium chloride. Some potassium perchlorate crystals also decompose giving a little oxygen and forming potassium chloride.

$$4KClO_3 = 3KClO_4 + KCl$$
$$KClO_4 = KCl + 2O_2.)$$

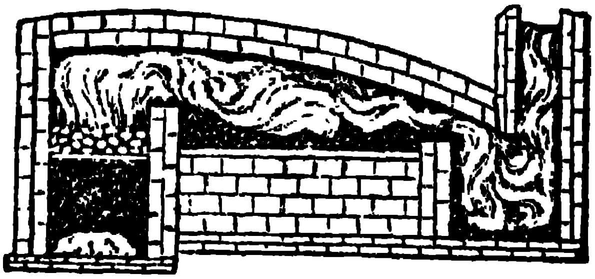
(*e*) The mass remaining after heating, when crystallised from hot water, gave crystals of potassium chlorate, $KClO_3$. Thus, the final product was potassium chlorate, $KClO_3$. [If, however the temperature would have been raised to 380°C. and the crystals of potassium chlorate kept at the temperature for some time and then the residue crystallised from hot water, the final product obtained would have been crystals of potassium perchlorate, $KClO_4$.]

Q. 4. *Give a neat sketch of a reverberatory furance and describe a method for the extraction of lead by its use.*

Write equations representing the changes involved.

Ans. The important ores of lead are

Galena—PbS
Anglesite—$PbSO_4$
Cerussite—$PbCO_3$.



Reverberatory Furnace

Fig 4.

Extraction :—

Lead is very easily obtained from its ores. It is chiefly extracted from galena, PbS. Galena is roasted on the hearth of a reverberatory furnace (see Fig. 4) in presence of air, when it is *partially* oxidised to lead oxide and lead sulphate.

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4.$$

A little quicklime is then added to the roasted mass and the temperature of the furnace is then raised to bright redness. The oxide and sulphate of lead act upon the unchanged lead sulphide with the production of metallic lead.

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

The lime forms a slag with the silica present in the ore.

Q. 5. *What is meant by 'hydride of an element'? Write names of the simplest hydrides of nitrogen, carbon, oxygen and sulphur.*

Describe the usual method for the preparation of the simplest hydride of sulphur and enumerate the changes that occur when this is allowed to come in contact with (a) caustic soda solution, (b) ferric chloride solution, (c) bromine and (d) lead nitrate solution.

Ans. The term 'hydride' of an element means a binary compound of hydrogen and the element. Thus, sodium hydride means a compound of sodium and hydrogen of the formula NaH.

The simpest hydride of nitrogen is ammonia, NH_3
,, ,, ,, carbon is methane, CH_4
,, ,, ,, oxygen is water, H_2O
,, ,, ,, sulphur is sulphuretted hydrogen,—H_2S.

The usual nomenclature of the above compounds is not the hydride of the elements, but in case of carbon the hydrogen compound is called a hydrocarbon, in case of oxygen it is named an oxide and in case of sulphur it is a sulphide.

Method of preparation of the simplest hydride of sulphur, viz., H_2S, sulphuretted hydrogen :—

Sulphuretted hydrogen is most conveniently prepared in the laboratory by the action of cold, dil. HCl or H_2SO_4 upon ferrous sulphide. For small quantites, Woulfe's bottle is used and for comparatively large quantities, Kipp's apparatus is employed.

The ferrous sulphide, FeS, in broken fragments, is introduced into the central globe of the Kipp's apparatus. The stop-cock is opened and dil. H_2SO_4 is poured down the safety funnel at the top till the liquid fills the lowest globe and then rises into the central globe. Here the acid comes in contact with FeS : sulphuretted hydrogen is produced and escapes through the stop-cock. The gas is collected by upward displacement of air.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

When the gas is not required, the stop-cock is closed ; the gas collects in the central globe, and the pressure of the gas forces the acid out of the central globe. The acid rises up the stem and goes to the topmost globe. Thus further reaction stops. When gas is required, the stop-cock is opened, H_2S escapes, the acid comes down from the topmost globe and so the contact between FeS and H_2SO_4 is brought about. Hence fresh quantites of H_2S are evolved.

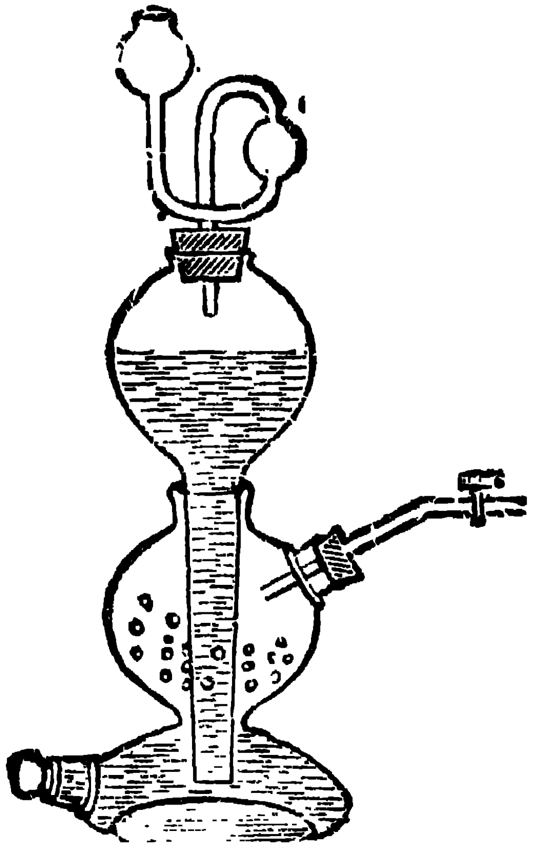


Fig. 5

(*a*) When sulphuretted hydrogen is passed into caustic soda solution, at first sodium sulphide is formed in solution, so long as caustic soda is in excess.

$$2NaOH + H_2S = Na_2S + 2H_2O.$$

But when H_2S is passed in excess, sodium hydrogen sulphide is formed in solution.

$$NaOH + H_2S = NaHS + H_2O.$$

With further excess of sulphuretted hydrogen, sodium polysulphides, Na_2S_x, are produced.

(*b*) When sulphuretted hydrogen is allowed to come in contact with ferric chloride solution, ferric chloride is reduced to ferrous chloride, and sulphur is precipitated. Hydrochloric acid is also formed, which, along with ferrous chloride, remains in solution.

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

(*c*) When sulphuretted hydrogen is allowed to come in contact with bromine, hydrobromic acid is formed and the colour of bromine is discharged. Sulphur is also precipitated. Bromine oxidises suphuretted hydrogen to sulphur and is itself reduced to hydrobromic acid. Thus a turbid, colourless solution of HBr, containing precipitated sulphur, is obtained.

$$H_2S + Br_2 = 2HBr + S.$$

(*d*) When sulphuretted hydrogen is allowed to come in contact with lead nitrate solution, a black precipitate of lead sulphide is formed along with nitric acid produced in solution. The nitric acid formed oxidises some H_2S to S which is precipitated.

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3.$$

Q. 6. *Name at least four important ores of copper and write their formulæ.*

Describe some method for preparing refined copper from any of its ores and discuss the changes involved in the process.

Ans. Important ores of copper are :

(1) Ruby ore, Red copper ore or cuprite, Cu_2O.
(2) Copper glance, Cu_2S.
(3) Covellite or indigo copper, CuS.
(4) Copper pyrites, Cu_2S, Fe_2S_3 or $CuFeS_2$.
(5) Erythrite or purple copper ore, $3Cu_2S$, Fe_2S_3.
(6) Malachite, $CuCO_3$, $Cu(OH)_2$.
(7) Azurite, $2CuCO_3$, $Cu(OH)_2$.

Refined copper can be prepared either from its oxide or carbonate ores as also from its sulphide ores. The method of preparation depends on the nature of the ore. In the cases of the oxide and carbonate ores of copper, the ore is first subjected to calcination, whereby cupric oxide is formed.

$$CuCO_3, Cu(OH)_2 = 2CuO + CO_2 + H_2O.$$
$$2Cu_2O + O_2 = 4CuO.$$

The oxide of copper so formed is then mixed with anthracite or coke and a little sand (sand being added to act as a flux), and the mixture is heated strongly in a *blast furnace* whereby the oxide is reduced to the metal.

$$Cu_2O + C = 2Cu + CO$$
$$CuO + C = Cu + CO$$
$$CuO + CO = Cu + CO_2.$$

The flux combines with the impurities and form a fusible slag. The molten slag is run off and copper produced is taken out. Copper thus obtained is then refined by either the *poling process* or the electrolytic process described below.

From its sulphide ore, viz. copper pyrites, copper is extracted by a thermal process described in the following :—

At first the ore is concentrated either by gravity separation or by Floatation process. For this purpose the ore is first crushed and finely powdered. The powdered ore is next churned with water containing a little pine oil, Xanthate and lime, by blowing air through the mixture. By this operation a froth is produced, which carries up along with it the particles of copper ore, these being preferentially wetted by oil, leaving sand and other impurities at the bottom, since they are preferentially wetted by water. The froth is collected by skimming and allowed to settle.

The concentrated ore is next roasted in a multiple-hearth furnace, so that the ore gradually descends from hearth to hearth. By this operation some of the sulphur in the ore is burnt to sulphur dioxide, which escapes as gas, and the metals, viz., iron present in pyrites and copper are partially oxidised.

$$Cu_2S.Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S.Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2,$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

this last reaction occurring only to a very small extent. The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when a little quantity of Cu_2O formed in the previous operation reacts with iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced in the previous operation reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained of cuprous and ferrous sulphides is known as *matte.* The molten matte is then directly run into a Bessemer converter with a little silica and a blast of air is introduced through tuyeres placed at the sides. Iron is first oxidised to FeO which combines with silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued. Cu_2S is then partially oxidised to Cu_2O and this Cu_2O reacts with unchanged Cu_2S to form copper and SO_2. The slag is removed, the blast stopped and the converter tilted to pour off Cu. This copper has a blistered appearance due to escape of SO_2.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

Blistered copper is then melted on the hearth of a reverberatory furnace when the impurities are oxidised. Some escape as gas, others form slag with the furnace lining of silica, which is removed. Next the metal begins to oxidise. Anthracite coal is then sprinkled on the molten mass and the mass is stirred with logs of green wood. When the copper attains the requisite *tough-pitch*, it is poured out.

Electrolytic refining of copper is carried out in the following way :—

Thick sheets of impure copper (even of blister copper before it is thermally refined) are suspended from a metal rod which is connected to the positive pole of a battery, thus making those thick sheets function as anodes, in a bath of copper sulphate solution *acidified* with dilute H_2SO_4 taken in a wooden vessel lined with lead.

Thin plates of pure copper are suspended in the same bath from another metal rod connected to the negative pole of the battery, thus making those thin sheets function as cathodes, and these thin plates are inserted alternately between the thick sheets. On passing electric current through the bath of copper sulphate, the thick sheets gradually pass into solution and pure copper is deposited on thin plates. Impurities present either pass into solution or are deposited at the bottom of the bath near the anode as anode mud. Copper, thus obtained at the cathode is 99·99 per cent. pure.

Q. 7. *Indicate the methods for the preparation of :—*

(*a*) *Anhydrous aluminium chloride from scrap aluminium,*

(*b*) *Lunar caustic from silver glance,*

(*c*) *Corrosive sublimate from mercuric sulphate and*
(*d*) *Mosaic gold.*

Ans. (*a*) Scrap aluminium is to be taken in a hard glass tube fitted with corks at two ends through which glass tubes pass. The hard glass tube containing scrap Al is then connected with the help of glass tube at one end to a dry hydrogen chloride generator and the glass tube at other end is dipped into a dry glass flask. The hard glass tube is next heated and the current of dry hydrogen chloride is passed over heated scrap Al. Anhydrous aluminium chloride formed sublimes off and collects in the dry glass flask. Hydrogen gas evolved passes away.

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

(*b*) Silver glance is naturally occurring silver sulphide, Ag_2S. Lunar caustic is silver nitrate, $AgNO_3$. Now, naturally occurring silver glance, Ag_2S, cannot be directly converted into silver nitrate by treating with nitric acid. So, at first metallic silver is produced from silver glance by the cyanide process. Silver glance is finely crushed and is treated with a dilute solution of sodium cyanide in water and a current of air is passed through the solution. Sodium cyanide dissolves the silver sulphide present in silver glance forming soluble sodium argento-cyanide. The silver is now precipitated from the filtered solution by the addition of sodium sulphide as silver sulphide. This precipitated silver sulphide is reduced by scrap aluminium and caustic soda solution.

$$\begin{aligned} Ag_2S + 4NaCN &= 2NaAg(CN)_2 + Na_2S. \\ 2NaAg(CN)_2 + Na_2S &= 4NaCN + Ag_2S \\ Ag_2S + 2H &= 2Ag + H_2S. \end{aligned}$$

This precipitated silver is removed by filtration, washed thoroughly with water and then dissolved in warm moderately dilute nitric acid when silver nitrate solution is obtained. The solution is evaporated to crystallisation and cooled, when crystals of silver nitrate, lunar caustic, is obtained.

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O.$$

(*c*) For preparation of corrosive sublimate, $HgCl_2$, from mercuric sulphate, a mixture of mercuric sulphate and common salt with a little manganese dioxide is taken in a long-necked flat-bottomed flask and heated on a sand-bath. MnO_2 is added to prevent reduction of $HgCl_2$ formed to calomel by organic matter present in common salt.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

After the reaction is over, the flask is cooled and then broken. The cake of mercuric chloride, formed as a deposit inside the flask, is removed. It is then dissolved in water by heating and crystallised therefrom. The purification is carried out by recrystallisation from water solution.

(*d*) Mosaic gold is a special type of stannic sulphide obtained by some heat-treatment and is different from precipitated stannic sulphide.

It is prepared in the dry way as golden scales by heating tin-amalgam, sulphur and ammonium chloride in a retort when golden yellow scales are obtained as a sublimate.

$$Sn + 4NH_4Cl = (NH_4)_2 SnCl_4 + H_2 + 2NH_3$$
$$2(NH_4)_2SnCl_4 + 2S = SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl.$$

1942

FIRST PAPER

Q. 1. *State the fundamental postulates of Dalton's atomic theory and show that the three laws of chemical combination can be easily deduced from the theory.*

Ans. The fundamental postulates of Dalton's Atomic theory are :

(*i*) Matter is composed of *minute indivisible* particles called atoms, which can neither be created nor destroyed by any chemical process.

(*ii*) Atoms of the same element are similar in properties in all respects and are equal in weight.

(*iii*) Atoms of different elements have different properties and different weights.

(*iv*) Chemical combination between two or more elements takes place by the union or juxtaposition of the atoms of those elements in simple numerical proportions, *viz.*, 1 : 1, 1 : 2, 2 : 1, or 2 : 3, etc.

(*v*) The combining weights of the elements represent the combining weights of the atoms of different elements concerned.

Dalton's Atomic Theory explains the laws of chemical combination by weight, but it fails to explain the law of combining volumes of gases as propounded by Gay Lussac.

We shall here see how the laws of chemical combination are explained with the help of this theory.

(1) *Law of conservation of Mass.*—Since matter is made of atoms which cannot be created, destroyed or divided, the total number of atoms present at the beginning of a chemical change must also be present at the end of it, provided it is not allowed to escape from the region of reaction. Again, since each atom has a fixed mass, the total mass present at the beginning of a chemical reaction remains the same after the reaction. Thus the statement of the law, *viz.*, in a chemical change the total mass of the reacting substances is equal to the total mass of the products, is explained easily from Dalton's Atomic Theory.

(2) *Law of Definite Proportions.*—When elements combine to form a compound, the combination takes place through their atoms that unite. Let us suppose that x atoms of an element A combine with y atoms of another element B to form a molecule of the compound of A and B. The weights of the elements A and B present in such a compound are in the ratio $x \times$ at. wt. of $A : y \times$ at. wt. of B. But the atomic weights of A and B are fixed, and in the compound of A and B, these two elements are present in a fixed ratio. Thus the statement that the same compound always contains the same elements, combined together in the some proportion by weight, is found to be deducible from Dalton's Atomic Theory.

(3) In explaining the *law of multiple proportions* from the postulates of Dalton's Atomic theory, let us assume that two elements A and B combiue together to give more than two different compounds. Let us also assume that the simplest compound formed from A and B contains 1 atom of A and 1 atom of B, so that its formula is AB. Since atoms are indivisible and compounds are formed by the union of atoms in simple numerical proportions, 1 or more atoms of A will now combine with 2 or more atoms of B to give the other compounds of A and B. Let the formula for *another* compound of A and B be AB_2 and yet a third compound of A and B is found whose formula is A_2B_3. Let us assume that atomic weights of A and B be m and n respectively. Then we find that

(*i*) In the first compound AB,

n parts by weight of B have combined with m parts by weight of A.

(*ii*) In the second compound AB_2,

$2n$ parts by weight of B have combined with m parts by weight of A.

i.e., n parts by weight of B have combined with $\frac{m}{2}$ parts by weight of A.

(*iii*) In the compound A_2B_3,

$3n$ parts by weight of B have combined with $2m$ parts by weight of A.

i.e., n parts by weight of B have combined with $\frac{2m}{3}$ parts by weights of A.

Therefore, the weights of A which combine with a constant weight of B, *viz.*, n, are as $m : \frac{m}{2} : \frac{2m}{3}$, or as $1 : \frac{1}{2} : \frac{2}{3}$ or as 6 : 3 : 4, which is a simple ratio. Hence it is seen that the law of multiple proportions follows as a necessary corollary from Dalton's Atomic theory.

(4) *Law of Reciprocal Proportions.*—Let us suppose that a, b and c are the at. wts. of three elements A, B and C respectively. And let one atom of A combine with one atom of B to form a molecule of the compound AB and one atom of A combine with one atom of C to form a molecule of the compound AC.

(*i*) If now combination between B and C be possible, they will form a compound, either by combination of one atom of B with one atom of C in which case the weights in which B and C combine will be as $b : c$., *i.e.*, in the same ratio in which they combine separately with A, or (*ii*) since atoms are indivisible, x atoms of B may combine with y atoms of C where x and y are simple integers ; in that case the weights of B and C shall be in the ratio $(b \times x) : (c \times y)$ *i.e.*, B and C combine together in weights which are simple multiples of their weights in which they separately combine with A.

Law of Reciprocal Proportions is stated thus :

If a certain weight x of an element A combine with a certain weight y of an element B and a certain weight z of an element C, then, if combination between B and C be possible, they will combine in the ratio $y : z$ or in some simple multiple of this ratio, *viz.* $2y : z$, or $z : 2y$, or $2y : 3z$, etc.

Q. 2. *A gaseous mixture contains 50% hydrogen, 40% methane and 10% oxygen. Calculate the volume of additional oxygen at N. T. P. that will be required for the complete combustion of 200.c.c. of the above gaseous mixture measured at 27°C. and 750 mm. pressure.*

What amount of potassium chlorate is to be decomposed by heat in order to generate the required quantity of oxygen.
$(K = 39{\cdot}1,\ Cl = 35{\cdot}5,\ O = 16{\cdot}0)$.

Ans. Since the gaseous mixture contains 50% hydrogen,

$\therefore$ 200 c.c. of the mixture will contain 100 c.c. of hydrogen.

Again, since the gaseous mixture contains 40% methane,

$\therefore$ 200 c.c. of the mixture will contain $\frac{200 \times 40}{100}$ or 80 c.c. of methane.

Since 10% of the mixture is oxygen, 200 c.c. of the mixture contains $\frac{10 \times 200}{100}$ or 20 c.c. of oxygen.

Now, from the equation $\underset{2\text{ vols.}}{2H_2} + \underset{1\text{ vol.}}{O_2} = 2H_2O$; we know that 2 vols. of hydrogen require 1 vol. of oxygen for complete combustion measured under the same conditions of temp. and pressure ; therefore, 100 c.c. of hydrogen will require 50 c.c. of oxygen for complete combustion.

Again, from the equation $\underset{1\text{ vol.}}{CH_4} + \underset{2\text{ vols.}}{2O_2} = CO_2 + 2H_2O$, we know that 1 vol. of methane requires 2 vols. of oxygen for complete combustion measured at same temp. and pressure ; therefore 80 c.c. of methane will require 160 c.c. of oxygen for complete combustion. Therefore, for complete combustion of hydrogen and methane present in the gaseous mixture, total volume of oxygen required is (50 + 160) or 210 c.c. at 27°C., and 750 mm. But the gaseous mixture contains 20 c.c. of oxygen in itself. Therefore the volume of additional oxygen required for the complete combustion of hydrogen and methane present in the gas mixture = (210 − 20) or 190 c.c. Now, 200 c.c. of the gaseous mixture was measured at 27°C. and 750 mm. pressure. Therefore 190 c.c. of additional oxygen required is also measured at 27°C. and 750 mm. pressure. Let V be the volume of this oxygen at N.T.P., *i.e.* at 0°C. and 760 mm. pressure. Then by Boyle's and Charles' laws we have

$$\frac{190 \times 750}{273 + 27} = \frac{V \times 760}{273}$$

$$\text{whence } V = \frac{190 \times 750 \times 273}{760 \times 300} \text{ c.c.}$$

$$= 170{\cdot}6 \text{ c.c.}$$

Again, from the equation

$$2KClO_3 = 2KCl + 3O_2$$

$$2 \times (39{\cdot}1 + 35{\cdot}5 + 48) \qquad 3 \times 32$$

$$\text{or, } 2 \times 122{\cdot}6$$

We know that, 3 × 32 grams of oxygen can be obtained from 2 × 122·6 grams of potassium chlorate. But since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P., 3 × 22·4 litres of oxygen at N.T.P. can be obtained by the decomposition of 2 × 122·6 grams of potassium chlorate. Therefore, 1 c.c. of oxygen at N.T.P. can be obtained by the decomposition of $\frac{2 \times 122{\cdot}6}{3 \times 22{\cdot}4 \times 1000}$ grams of $KClO_3$. Hence 170·6 c.c. of oxygen at N.T.P. can be obtained by the decomposition of $\frac{2 \times 122{\cdot}6 \times 170{\cdot}6}{3 \times 22{\cdot}4 \times 1000}$ grams, or 0·6227 gram of $KClO_3$.

Q. 3. *Describe experiments to determine the composition of hydrochloric acid gas both by analysis and synthesis of the substance.*

Why is the determination by the method of analysis alone not regarded as a sufficient and rigorous proof of its composition ?

Ans. The **analytical method** for the determination of the composition of hydrochloric acid gas consists of two sets of experiments :—

(1) Electrolysis of concentrated solution of hydrochloric acid :—

(*i*) Strong hydrochloric acid solution is taken in Hoffmann's apparatus which consists of a three-limbed glass vessel, the two side-tubes of which are provided with a stop-cock each at the top and the middle limb is provided with a bulb at the top, which serves as a reservoir. (*ii*) The two side limbs are provided with two carbon electrodes fitted at the bottom through two rubber stoppers. The carbon electrodes are connected to the terminals of a battery. (*iii*) Now the apparatus is filled up completely with concentrated hydrochloric acid. (*iv*) Next electric current is passed through the liquid. Hydrochloric acid is decomposed and hydrogen is liberated at the cathode and chlorine at the anode. Hydrogen collects in the limb containing the cathode, but chlorine liberated in the limb containing the anode dissolves in the water present in concentrated hydrochloric acid and so no gas collects in that limb for some time. (*v*) When the liquid in the limb containing the anode becomes saturated with the chlorine evolved, both the stop-cocks are opened to drive out all gases and to refill the limbs with concentrated hydrochloric acid. (*vi*) After the gases are driven off, the stop-cocks are closed and electrolysis is allowed to proceed on. This time it is found that the gases collect in equal volumes in the two limbs. The volume of *hydrogen* collecting in the limb carrying the cathode (which is identified by the facts that it burns in oxygen giving water alone and that it is absorbed by palladium) is equal to the volume of *chlorine* collecting in the limb carrying the anode (which is identified by its greenish-yellow colour, smell of bleaching powder and capacity of turning starch-iodide paper blue).

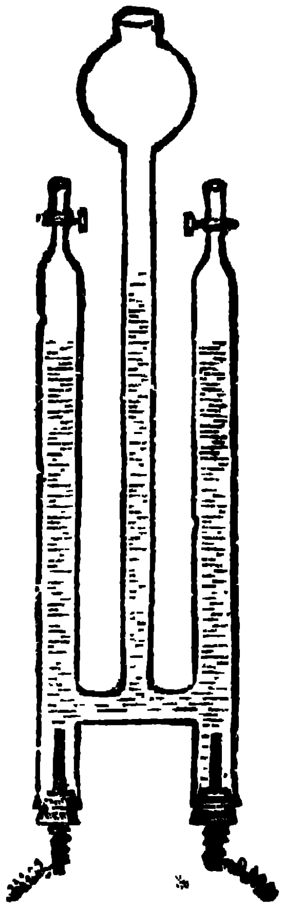


Fig. 6

Thus it is established that hydrochloric acid gas contains equal volumes of hydrogen and chlorine.

(2) *Sodium Amalgam method for establishing that hydrochloric acid gas contains half its volume of hydrogen :—*

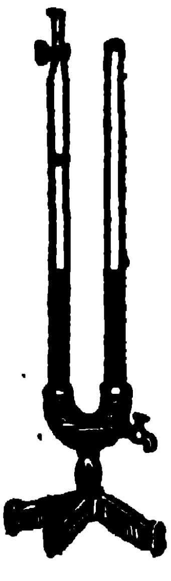


Fig. 7

(*i*) In a *U*-shaped glass tube provided with a stop-cock at one end and opened at the other end, with a tap near the bend, dry hydrochloric acid gas is collected from a generating apparatus by displacement of mercury into the closed limb by opening the stop-cock and the tap after filling the *U*-tube completely with mercury. (*ii*) The stop-cock and the tap are closed and the mercury in both the limbs is brought to the same level by opening the tap and the volume of hydrochloric acid gas taken is divided into two halves by a rubber ring placed at the middle position as shown in the figure. (*iii*) The open limb is then completely filled with sodium amalgam and mercury. (*iv*) This limb is now closed with a rubber stopper and hydrogen chloride is carefully transferred from the closed limb to the other limb several times till the action is complete. Sodium chloride is formed and the residual gas is completely transferred to the closed limb.

$$2Na + 2HCl = 2NaCl + H_2.$$

(*v*) Mercury level is next adjusted again by letting out mercury through the tap when the level of mercury is found to coincide with the rubber ring. This proves that volume of the gas remaining is exactly equal to half the volume of hydrochloric acid gas taken.

(*vi*) That the residual gas is hydrogen is proved by the facts that it burns in air giving water alone and that it is absorbed by palladium.

This proves that hydrogen chloride contains half its volume of hydrogen.

These two experiments together prove that *two volumes* of hydrochloric acid gas contain *one volume* of hydrogen and *one volume* of chlorine.

Synthetic method :—of determining the composition of hydrochloric acid gas :

(*a*) A stout glass explosion tube, consisting of two bulbs provided with stoppers at two ends and connected together by means of a three-way stop-cock at the middle, is taken. The two bulbs are of exactly equal volumes (Fig. 8, upper tube).

(*b*) One of the bulbs is filled up with chlorine either by displacement of air keeping the three-way stop-cock open or by displacement of brine. (*c*) The other bulb is then filled up with hydrogen in the same manner by keeping the three way stop-cock open to the air. (*d*) The three-way stop-cock is then turned the other way so that the two bulbs are put into communication and the two gases are allowed to mix, the mixing being carried out in the dark. (*e*) The mixture is then exposed to diffused sunlight for a certain length of time to allow the reaction to be completed. The two gases combine to give hydrochloric acid gas. (*f*) The tube is cooled and one of the end stop-cocks is dipped under mercury and opened. No gas enters or leaves the tube, nor does mercury rise in the tube. This proves that there has been no change in volume as a result of the combination of the two gases. (*g*) Water is then poured over mercury, and the tube is raised so that the open stop-cock dips into water only. Water then rushes up and completely fills the tube, due to the whole quantity of gas dissolving in water. (*h*) The solution so formed on being tested, is found to be acidic to litmus and it gives a *curdy white ppt.* with silver nitrate solution ; the precipitate is insoluble in conc. HNO_3, but readily dissolves in NH_4OH. After the reaction, therefore, the tube contains only hydrochloric acid gas.

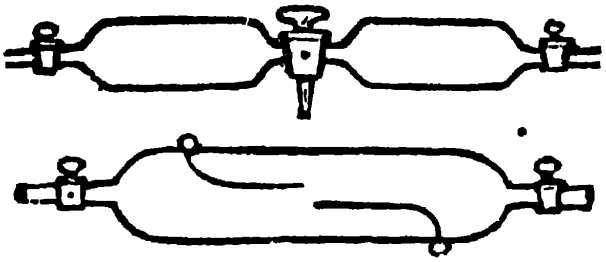


Fig. 8

This proves that *1 volume of hydrogen combining with 1 volume of chlorine produces 2 volumes of hydrochloric acid gas.*

Synthesis of hydrochloric acid gas from the constituent elements, hydrogen and chlorine, may also be effected by passing electric spark through the mixture of the two gases taken in equal volumes (produced by the electrolysis of conc. hydrochloric acid and collected after the liquid becomes satuarated with chlorine by drying with a $CaCl_2$—tube) in a tube indicated in the lower position of the adjoining figure. This leads to the same result as above.

1 vol. of hydrogen combines with 1 vol. of chlorine to produce 2 vols. of hydrogen chloride. This is the result of analysis of hydrogen chloride. Now, if we suppose, that 1 vol. of hydrogen contains n molecules, then by Avogadro's hypothesis we come to know that n molecules of hydrogen combine with n molecules of chlorine to produce $2n$ molecules of hydrogen chloride. Dividing by n, 1 molecule of hydrogen combines with 1 molecule of chlorine to give rise to 2 molecles of hydrochloric acid gas. But since it is known that hydrogen molecules as also chlorine molecules are diatomic, we get that 2 atoms of hydrogen combine with 2 atoms of chlorine to produce 2 molecules of hydrogen chloride. Therefore, 1 atom of hydrogen and 1 atom of chlorine by combination give rise to 1 molecule of hydrochloric acid gas. Thus the formula for hydrochloric acid gas is HCl. This formula is confirmed by the determination of the density of hydrochloric acid gas. This is found by experiment to be 18·25 and so by application of Avogadro's hypothesis, the molecular weight of hydrogen chloride is 36·5. This tallies with the formula HCl.

Now, by analysis, we get only the atomic ratio in the molecule. Elements combine in forming a compound in the proportion of their equivalent weights. But the combination in elements is also determined by the valencies of the elements. So by analysis the combining weights alone being obtainable, we cannot determine the composition of the compound therefrom. To get the molecular formula from the empirical formula obtainable from analysis, we must have the knowledge of its gaseous density. Along with that we should have also the knowledge of valencies of the elements combining.

Hence the method of analysis alone is not regarded as a sufficient and rigorous proof of the composition of hydrogen chloride.

Q. 4. *How would you prepare a saturated solution of hydriodic acid in the laboratory? Draw a neat sketch of the apparatus you would use and give equations for the reactions that occur.*

Explain what happens when a solution of hydriodic acid is (a) exposed to air for a long time, (b) mixed with chlorine water, and (c) treated with a solution of hydrogen peroxide.

Ans. In the laboratory hydriodic acid is prepared by dropping water from a dropping funnel, fitted to a flask containing a mixture of red phosphorus and iodine. The flask is provided with a delivery tube and the delivery tube is connected to a *U*-tube containing glass beads and moist red phosphorus. The flask is cooled by dipping it in water. Hydriodic acid gas mixed with iodine vapour is evolved in the flask and in passing through the U-tube containing moist red phosphorus, iodine vapour is absorbed. The HI gas is then collected by upward displacement of air.

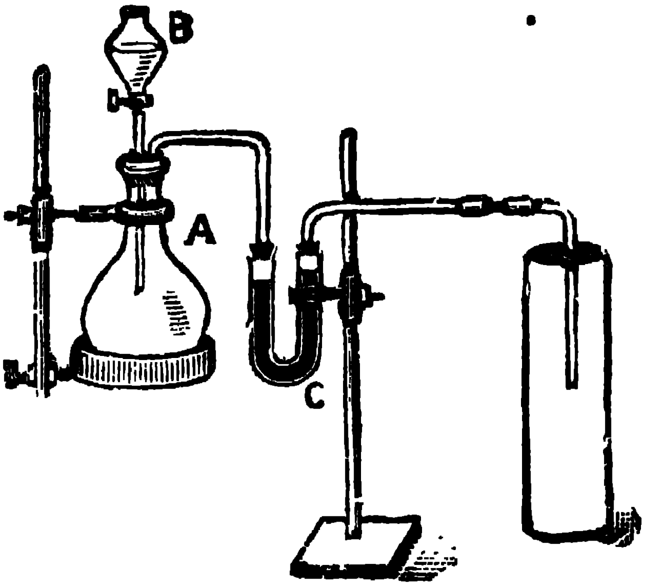


Fig. 9

At first phosphorus tri-iodide is formed, which is then decomposed by water forming phosphorus acid and hydriodic acid.

$$P + 3I = PI_3. \quad PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

A saturated solution of hydriodic acid can be obtained by joining the delivery tube to the stem of a funnel and then dipping the mouth of the funnel just below the surface of water contained in a beaker. By this inverted funnel arrangement, as it is called, the back suction is prevented and gradually a saturated solution can be prepared.

A solution of HI in water can be conveniently prepared by passing H_2S or SO_2 through water containing Iodine in suspension.

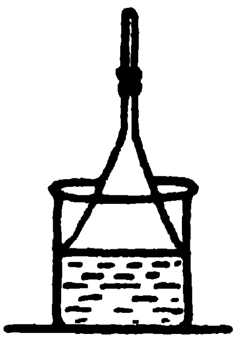


Fig. 10

$$H_2S + I_2 = 2HI + S$$

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

The water solution is prepared to saturation, then it is filtered and the filtrate is distilled. The distillate so obtained is a solution of HI in water.

(*a*) When hydriodic acid solution is exposed to air for a long time, it is oxidised by atmospheric oxygen with the production of water and liberation of iodine. This liberated iodine dissolves in HI solution remaining unoxidised, producing brown solution.

$$4HI + O_2 = 2H_2O + 2I_2.$$

(*b*) When mixed with chlorine water, hydriodic acid solution decomposes liberating iodine which is deposited in the form of solid flakes.

$$2HI + Cl_2 = 2HCl + I_2.$$

(*c*) When treated with a solution of hydrogen peroxide, hydriodic acid solution is oxidised and iodine is liberated and water is formed.

$$2HI + H_2O_2 = I_2 + 2H_2O.$$

Q. 5. *Describe the process of making sulphur trioxide on a large scale from sulphur dioxide. How is pure sulphuric acid prepared from sulphur trioxide ?*

Explain what happens when a limited quantity of cold water is added to concentrated sulphuric acid.

Give illustrations of the use of sulphuric acid as (*a*) *a dehydrating agent,* (*b*) *an oxidising agent.*

Ans. Sulphur trioxide is prepared on a large scale from sulphur dioxide by passing a mixture of sulphur dioxide and excess of oxygen in the form of air, freed from dust, sulphur particles, arsenious oxide, etc., and dried properly, through a contact furnace containing platinised asbestos heated by ring burners to a temperature of 450°C. at the start. The contact furnace consists of an iron box fitted with vertical iron pipes packed with the platinised asbestos. The heating is discontinued as the reaction proceeds, for the heat of the reaction

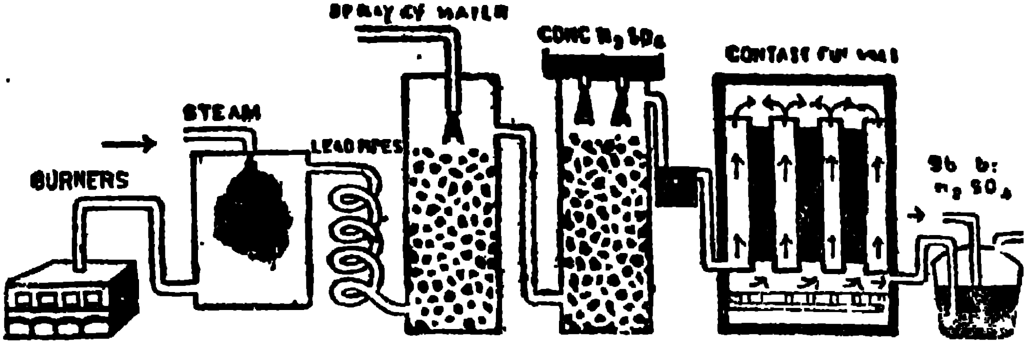


Fig. 11

maintains the temp. necessary for the reaction. Platinised asbestos acts as the catalytic agent and sulphur dioxide is oxidised to sulphur trioxide by atmospheric oxygen. A white cloud of sulphur trioxide escapes through the other side of the furnace. This white cloud is passed through a well-cooled receiver where sulphur trioxide condenses in the form of white silky needles.

$$2SO_2 + O_2 = 2SO_3.$$

Pure sulphuric acid can be prepared from sulphur trioxide by adding it to 98% sulphuric acid in which sulphur trioxide dissolves readily forming fuming sulphuric acid.

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

Then calculated quantity of water is added to it to produce 98% sulphuric acid.

$$H_2S_2O_7 + H_2O = 2H_2SO_4.$$

[N. B. Water cannot be used directly for absorbing sulphur trioxide for droplets of sulphuric acid are formed and that prevents further action.]

98% H_2SO_4 is then cooled by freezing mixture when crystals of pure H_2SO_4 melting at 10°C. are formed. These crystals are seperated from the adhering liquid and melted when 100% H_2SO_4 is obtained.

When a limited quantity of cold water is added to concentrated sulphuric acid, much heat is evolved. Heat produced is so great that water added is converted into steam with great speed and the steam along with sulphuric acid spurts out of the reaction vessel and so there is the chance of extreme danger to the experimenter. So it is always advised to add the concentrated acid in a thin steam to water with constant stirring. Sulphuric acid form hydrates like H_2SO_4, H_2O, $H_2SO_4, 2H_2O$ and $H_2SO_4, 4H_2O$ with water.

(*a*) Concentrated sulphuric acid is used as a desiccating agent for drying gases which do not react with it. It is also used in desiccators for keeping the atmosphere inside the desiccator dry. It is also capable of abstracting the elements of water from many organic compounds, *e.g.*, it abstracts elements of water from canesugar producing sugar charcoal.

$$C_{12}H_{22}O_{11} + H_2SO_4 = 12C + [11H_2O + H_2SO_4].$$

For this reaction to occur, concentrated sulphuric acid is added to a syrupy solution of sugar when the solution froths up due to escape of gases and it blackens due to separation of carbon.

(*b*) When carbon and sulphur are heated with conc. H_2SO_4, they are oxidised respectively to carbon dioxide and sulphur dioxide.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

Sulphuric acid also oxidises HI and HBr with the liberation of iodine and bromine respectively when heated.

$$2HI + H_2SO_4 = I_2 + 2H_2O + SO_2$$
$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2.$$

Q. 6. *Describe the preparation and properties of the following substances and state their uses :—*

(*a*) *Calomel,* (*b*) *White lead,* (*c*) *Plaster of Paris,* (*d*) *Green vitriol.*

Ans. (*a*) Calomel—Mercurous chloride, Hg_2Cl_2.

It is obtained as a curdy white precipitate when the solution of a soluble mercurous salt is treated with HCl or with the solution of a chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 + 2NaNO_3.$$

This substance is manufactured by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel. Hg_2Cl_2 sublimes off and condenses as a white cake in the upper part of the vessel. The sublimate is taken out and repeatedly boiled with water to free it completely from unchanged mercuric chloride, filtered and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Properties of calomel.—It is an amorphous white powder without any taste. It is insoluble in water and in dilute acids. It sublimes without decomposition when heated. It dissolves in aqua regia forming mercuric chloride. When treated with ammonia, it turns black due to the formation possibly of a mixture of finely divided mercury and amido-mercuric chloride, NH_2HgCl.

Use of calomel.—Calomel or mercurous chloride is used in medicine as a purgative.

(*b*) White lead, Basic lead carbonate, $2PbCO_3, Pb(OH)_2$.

Preparation of White lead : **Dutch Method** :—

Pieces of lead are placed in earthenware pots having perforated shelves near the bottom, on which lead rests. Dil. acetic acid (vinegar) is taken in the pots. The pots are now placed, one above the other, with alternate layers of spent tan-bark or horse-dung, inside a shed and the whole stack is left as such for about 5 to 6 weeks. CO_2 is formed due to fermentation of spent tan-bark or horse-dung and the heat generated during fermentation volatilises acetic acid which attacks lead giving basic lead acetate. Basic lead acetate is now decomposed by CO_2, producing basic lead carbonate (white lead) and free acetic acid. The acid attacks more lead converting it into white lead, and the cycle of changes is repeated. When lead is used up, the pots are taken down, the crust of white lead is detached, and is finely ground to separate it from any unchanged lead. It is now washed well with water and dried. The reactions occurring can be represented as follows :—

(1) $2Pb + 2H_2O + O_2 = 2Pb(OH)_2$.

(2) $Pb(OH)_2 + 2CH_3COOH = Pb(CH_3COO)_2 + 2H_2O$.

(3) $Pb(CH_3COO)_2 + Pb(OH)_2 = Pb(CH_3COO)_2, Pb(OH)_2$.

(4) $3[Pb(CH_3COO)_2, Pb(OH)_2] + 2H_2O + 4CO_2$
$= 2[2PbCO_3, Pb(OH)_2] + 6CH_3COOH$.

Properties.—

It is a white amorphous powder, insoluble in water. It has got an extensive covering power and is poisonous when taken into the system. It turns black by traces of H_2S present in air when it is used as a paint.

Uses.—

White lead is used as a white pigment on an extensive scale. It is usually used for oil paintings.

(*c*) Plaster of Paris, Calcium sulphate hemihydrate, $2CaSO_4, H_2O$.

It is prepared by heating gypsum, $CaSO_4, 2H_2O$ to a temperature not exceeding 120°C. in such a fashion that it does not come into contact with carbonaceous fuel to avoid reduction.

$$2CaSO_4, 2H_2O = (CaSO_4)_2, H_2O + 3H_2O.$$

Properties.—Plaster of Paris is a white powder. It sets to a hard mass with water. This is called *setting* of Plaster of Paris and it occurs due to re-hydration and reconversion into original gypsum—

$$2CaSO_4, H_2O + 3H_2O = 2(CaSO_4, 2H_2O).$$

Uses.—Plaster of Paris is used for preparing moulds in pottery works, surgical bandages and in preparing busts, statues, etc.

(*d*) Green vitriol, Ferrous sulphate heptahydrate, $FeSO_4, 7H_2O$.

Preparation.—Iron wire or ferrous sulphide is dissolved in dilute sulphuric acid, the solution filtered and the filtrate concentrated to crystallisation when green crystals of $FeSO_4, 7H_2O$ are obtained. This is manufactured by exposing heaps of marcasite (FeS_2) to air in the presence of moisture. The resulting sulphuric acid is treated with scrap iron and the mass is lixiviated with water. The solution so obtained is filtered and evaporated to crystallisation.

$$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4.$$

Green vitriol can be obtained as a by-product in the preparation of H_2S in the laboratory. The solution left behind in H_2S—Kipp, when filtered and concentrated, gives crystals of $FeSO_4, 7H_2O$.

Properties.—Green vitriol is a pale-green crystalline solid. It effloresces on exposure to air. It is soluble in water. It gradually turns brown due to oxidation into ferric sulphate by the atmospheric oxygen. When heated, it first gives the monohydrate, $FeSO_4, H_2O$, this on further heating to 300°C. in absence of air, gives the white anhydrous salt, $FeSO_4$. At a red heat, it decomposes giving Fe_2O_3, SO_2, and SO_3. $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. The water solution of ferrous sulphate absorbs nitric oxide giving the brown solution containing $FeSO_4, NO$.

Uses.—It is used in dyeing, in the preparation of jeweller's rouge and in manufacture of writing ink.

Q. 7 *Name important ores of aluminium. How is the metal extracted from its ore? Give a neat diagram of the furnace. State the uses of the metal.*

Ans. The principal ores of Aluminium are

(1) Bauxite, $Al_2O_3, 2H_2O$.
(2) Cryolite, $AlF_3, 3NaF$.

There are many naturally occurring compounds of Aluminium, but none of them can be considered as an ore of Aluminium, for none can be used for extracting the metal profitably and economically.

The extraction of aluminium consists of *two* operations :—(*a*) Purification of Bauxite which contains ferric oxide and silica as impurities and (*b*) electrolytic decomposition of purified Bauxite.

(*a*) Purification of Bauxite with the production of pure Al_2O_3 can be carried out in two ways. In the old process, (*a*) bauxite is heated to bright redness with sodium carbonate, when sodium aluminate, $NaAlO_2$, is formed. The mass is rapidly lixiviated with water, whereby a solution of sodium aluminate is obtained and finely divided ferric oxide, which remains insoluable, is removed by decantation. The clear solution of sodium aluminate is then treated with carbon dioxide at 50° – 60° when a granular precipitate of aluminium hydroxide is thrown down.

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2.$$
$$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3.$$

The precipitated $Al(OH)_3$ is separated and then ignited when Al_2O_3 is obtained.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

(*b*) In the modern Bayer process, the calcined bauxite is digested under 80 lb. pressure at 150°C. with caustic soda solution. Sodium aluminate is formed and oxide of iron is left behind. The solution of sodium aluminate is separated from deposited iron oxide by decantation and then agitated with precipitated alumina. Nearly all the alumina in solution is thereby precipitated, which is easily washed and this on ignition yields pure Al_2O_3.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O.$$

The above reaction is reversed on agitation with precipitated Al_2O_3.

The alumina purified by any of the above processes is then dissolved in fused cryolite and electrolysed between carbon electrodes. The electric furnace consists of an *iron box* lined internally with blocks of gas-carbon and is made the cathode. The anode consists of a bunch of carbon rods hung from a copper rod and dipped into the electrolytic bath. The electrolyte is a solution of purified Al_2O_3 in fused cryolite, AlF_3, $3NaF$, together with some fluorspar, CaF_2, the temperature of the bath being kept at 875° – 950°.

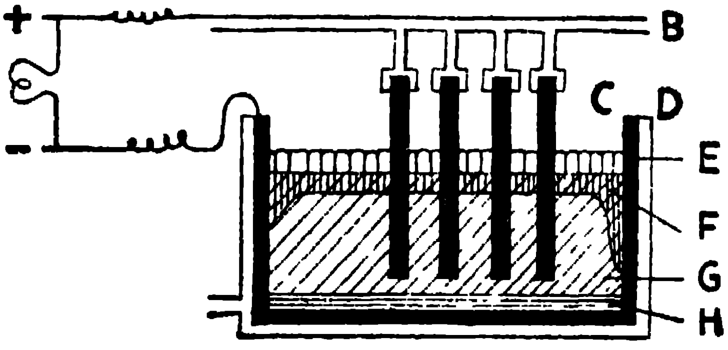


Fig. 12

The alumina is electrolysed, the metal being deposited at the bottom of the bath below the anodes. The oxygen liberated at the anodes attacks them with the production of CO and CO_2 in about equal volumes. The charge is usually covered with a layer of carbon and fresh alumina is stirred in from time to time. The complete decomposition of alumina is indicated by a rise in resistance of the bath, the lamp shunted with the bath brightening at this stage.

$$2Al_2O_3 = 4Al + 6O_2$$
$$C + O_2 = CO_2$$
$$2C + O_2 = 2CO.$$

The chief uses of the metal are—

(1) in the production of light alloys like magnalium, (Al + Mg), duralumin, (Al + Mg + Cu + Mn), aluminium bronzes, etc. ;

(2) in the production of aluminium powder which is used as a paint and in fireworks ;

(3) in the *thermite* process of the extraction of metals like Cr, Mn and for repairing iron rails ;

(4) in the production of amalgamated aluminium foil which is used as a reducing agent in neutral medium.

Q. 8. *Describe what happens when :—*

(*a*) *Supply of air is gradually increased or reduced in a Bunsen flame. Give reasons for your answer.*

(*b*) *An electric current is passed through a solution of copper sulphate and sodium chloride respectively.*

(*c*) *Lead nitrate and ferrous sulphate are separately heated. Give equations.*

Ans. (*a*) In a Bunsen burner, when the air-holes are kept closed and the burner lighted, the flame becomes luminous and consists of four zones :—

(*i*) The dark central zone containing unburnt gases.

(*ii*) The central luminous zone of incomplete combustion.

(*iii*) The faintly luminous outer zone. This zone is called the zone of complete combustion.

(*iv*) A small bright blue region at the base of the flame, which is non-luminous.

When the supply of air is gradually increased, the gas supplied, as it comes out of the jet and passes unburnt up the burner tube, sucks in air through the air-holes which are gradually opened to supply air. The gas mixed with air then burns at the mouth of the burner tube and the following changes in the flame are observed : (*a*) zone (*ii*) graduallybecomes smaller and ultimately disappears and the flames become non-luminous, (*b*) the flame is reduced in size, (*c*) zone (*iv*) gradually becomes continuous right up to the end like a cone. When the supply of air is increased to a great degree, this cone becomes green, the flame begins to roar and finally it strikes back, *i.e.*, the gas begins to burn at the jet instead of at the mouth of the burner tube. (*d*) The faintly luminous zone (*iii*) remains in tact. The flame now consists of practically two zones—(*i*) the inner blue zone containing unburnt gas inside and called the reducing zone and (*ii*) the outer pale blue zone of complete combustion, called the oxidising zone.

When the supply of air is gradually reduced by closing the air-holes, the above changes are observed in the reverse order gradually.

The changes are produced on account of diminished or increased oxidation of the gases (hydrogen and hydrocarbons) supplied through the burner tube. The flame becomes luminous, when the air supply is diminished, on account of separation of solid carbon particles due to incomplete combustion of the burner gases and for higher density of the gas supplied due to non-dilution with air. The non-luminosity of the flame, when the air-supply is increased, is due, on the other hand, to complete combustion in presence of excess of air, cooling due to mixing of gases supplied with cold air and lowering of density of gases due to dilution with air.

(*b*) On passing an electric current through a solution of copper sulphate, the solution undergoes electrolysis and copper ions are discharged at the cathode and sulphate ions at the anode. Metallic copper will be deposited at the cathode made of any metal, copper or platinum. But sulphate ion, which is discharged at the anode, attacks the anode if it be made of copper or any metal capable of being attacked by $SO_4{}^{=}$ion and no gas will be evolved ; but if the anode be made of platinum or any other metal incapable of reacting with $SO_4{}^{=}$ion, $SO_4{}^{=}$ion will react with water of the solution forming H_2SO_4 and evolving oxygen.

$$CuSO_4 = Cu^{++} + SO_4{}^{=}$$
$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

When an electric current is passed through a solution of sodium chloride, sodium is liberated at the cathode and chlorine at the anode. But sodium liberated at the cathode reacts with water present in the solution and forms caustic soda evolving hydrogen. So hydrogen is evolved as gas at the cathode.

$$2Na + 2H_2O = 2NaOH + H_2.$$

If the electrolysis be carried out in a divided cell like Castner-Kellner cell, caustic soda solution will be obtained in the cathode chamber from where hydrogen is also evolved and chlorine will be liberated as gas from the anode chamber. But if the electrolysis be carried out in an undivided cell, chlorine evolved at the anode will react with caustic soda produced forming sodium hypochlorite at the first instance, but if the electrolysis be carried out for sufficient length of time, sodium chlorate is the chief product.

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$
$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O.$$

(*a*) When lead nitrate crystals are heated, it first deprecipitates, then melts and then decomposes producing brown fumes of nitrogen peroxide, condensible to a yellow liquid on cooling in freezing mixture, and oxygen as gas and leaving a yellow residue of lead monoxide.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

When ferrous sulphate crystals, $FeSO_4, 7H_2O$, are heated, they lose water of crystallisation and at a red heat these decompose producing sulphur dioxide and sulphur trioxide and leaving a brown residue of ferric oxide (Jeweller's rouge).

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

1942

SECOND PAPER

Q. 1. *700 c. c. of gaseous hydrochloric acid measured at 0°C. and 760 mm. pressure were led into a solution of potassium hydroxide in water. After the reaction, the solution was still alkaline and required 55 c.c. of 1·2N sulphuric acid for its complete neutralisation.*

Calculate the quantity of potassium hydroxide present in the solution as also the potassium chloride formed.

Ans. We know that 22·4 litres of hydrogen chloride measured at 0°C. and 760 mm. pressure weigh 36·5 grams, since molecular weight of any gas expressed in grams occupy 22·4 litres at N.T.P.

Thus 22400 c.c. of gaseous hydrochloric acid at 0°C. and 760 mm. pressure weigh 36·5 grams.

∴ 700 c.c. of gaseous hydrochloric acid at 0°C. and 760 mm. pressure weigh $\frac{36{\cdot}5}{22400} \times 700$ grams $= 1{\cdot}1406$ grams.

Now, from the equation,

$$\begin{array}{cccc} KOH & + & HCl = KCl & + H_2O \\ 39+16+1 & & 36{\cdot}5 \quad 39+35{\cdot}5 & \\ \text{or} & & \text{or} & \\ 56 & & 74{\cdot}5 & \end{array}$$

We know that

36·5 grams of HCl can react with 56 grams of KOH and produce 74·5 grams of KCl.

Therefore, 1·1406 grams of HCl can react with $\frac{56}{36{\cdot}5} \times 1{\cdot}1406$ grams or 1·75 grams of KOH and produce $\frac{74{\cdot}5}{36{\cdot}5} \times 1{\cdot}1406$ grams or 2·3275 grams of KCl.

Again, 1000 c.c. of (N)H_2SO_4 solution contain 49 grams of sulphuric acid.

Therefore, 1000 c.c. of 1·2(N)H_2SO_4 solution contain 49 × 1·2 grams of sulphuric acid.

Hence, 55 c.c. of 1·2(N)H_2SO_4 solution contain $\frac{49 \times 1{\cdot}2}{1000} \times 55$ grams or 3·234 grams of sulphuric acid.

Now, from the equation

$$\begin{array}{llll} 2KOH & + & H_2SO_4 = K_2SO_4 + 2H_2O \\ 2 \times 56 & & 98 \end{array}$$

we know that

98 grams of H_2SO_4 will react with 2 × 56 grams of KOH.

Therefore, 3·234 grams of „ „ $\frac{2 \times 56}{98} \times 3{\cdot}234$ grams.

or, 3·696 grams of KOH.

Hence total quantity of KOH present in the solution = (1·75 + 3·696) or, 5·446 grams.

And potassium chloride formed = 2·3275 grams.

Q. 2. *What is understood by 'Periodic Classification of Elements'. How has this helped in the systematisation of Inorganic Chemistry? Illustrate your answer by an example.*

Ans. When the methods of determining atomic weights came to be established on firm grounds, there arose the possibility of comparing the atomic weights of elements and their properties, in order to find out some definite relationship between these two. As early as 1817, Dobereiner noticed that in some allied elements, the atomic weights were approximately in arithmetical progression. Thus

Ca......40		Li......7		S......37	
	48		16		47
Sr......88		Na... · 23		Se......79	
	49		16		48
Ba 137		K..... 39		Te 127	

These were called *Dobereiner's Triads.*

Almost half a century later, in 1864, the English Chemist Newlands made a remarkable observation that if elements were arranged in the ascending order of their atomic weights, counting from any one of them, the eighth member would be analogous in properties. This was called by Newlands the "**Law of Octaves**" from the analogy with the musical scale.

In 1869 Lothar Meyer, a German Chemist, and simultaneously, but quite independently, the Russian Chemist, Mendeleeff discovered that when the elements are arranged in the order of increasing atomic weights, their properties vary from member to member in a definite way, but return more or less to the same value at fixed points in the series.

If the sixteen elements with lowest atomic wts., after hydrogen, be arranged in order of increasing atomic wts. in two horizontal rows of eight, some of these relations will be recognised—

He = 4, Li = 7, Be = 9, B = 11, C = 12, N = 14,
O = 16, F = 19.
Ne = 20, Na = 23, Mg = 24, Al = 27, Si = 28, P = 31,
S = 32, Cl = 35·5.

In traversing from He to F in the upper row, we meet with certain characteristic properties belonging to each member, and also a certain gradation in those properties that are common. Coming to the second row, many of the characteristic properties of the members of the first row again appear, and the same regular modulation is met with in passing along the series: thus helium exhibits a likeness to neon, lithium resembles sodium, carbon corresponds to silicon, fluorine to chlorine. These resemblances are seen both in the physical as well as in the chemical properties of the elements, thus lithium and sodium are both soft white metals, and are strongly electro-positive. Fluorine and chlorine are both pungent corrosive gases, and are intensely electro-negative, while helium and neon are neither electro-positive nor electro-negative, have no chemical properties whatever, and therefore no valency.

Regarding then the eight elements of the first row as a period, we find that the various properties exhibited by the several members are met with again in those of the second period.

Not only do the properties of the elements themselves re-appear but also those possessed by the various compounds they form—thus lithum chloride ($LiCl$) and sodium chloride ($NaCl$) strongly resemble one another. The oxides of beryllium and magnesium (BeO and MgO) have similar properties. The compounds of fluorine and chlorine with hydrogen (HF and HCl) resemble each other, and so on.

This periodic re-appearance of similar properties, exhibited by the elements and their compounds as the atomic weights of the former gradually increase, is thus stated by Mendeleeff in his **Periodic Law** :—*The properties of the elements, as well as the properties of their compounds form a periodic function of their atomic weights.*

When the tabulation of the elements on his basis is continued after the completion of the second period with chlorine, it will be seen that, beginning with argon, eighteen elements have to be arranged before we meet with the re-appearance of those properties that belong to the first :—

A	K	Ca	Sc	Ti	V	Cr	Mn	(Fe	Co	Ni)
40	39	40	45	48	51	52	55	56	59	59
		Cu	Zn	Ga	Ge	As	Se	Br		
		63·5	65	70	72	75	79	80		

This constitutes what is known as a *long period*, incontradistinction to the two first, which are distinguished as *short periods*. In certain respects, however, the last seven elements in this long period exhibit certain amount of resemblances to the seven in the first portion (counting after Argon) ; that is to say, the properties displayed by the members of the first short period, which is known as the *typical period*, re-appear twice over in the long period. The three elements within the brackets are termed by Mendeleeff *transitional elements.*

Continuing the arrangement from bromine, another long period occurs, again containing three transitional elements —

Kr	Rb	Sr	Y	Zr	Cb	Mo		(Ru	Rh	Pd)
83	85	87·6	89	90·7	93·5	95	—	101	103	106
		Ag	Cd	In	Sn		Sb	Te	I	
		108	112	115	119		121·7	127·5	126·9	

After Iodine comes Xenon and then beginning with Xenon, thirty-two elements have to be traversed before we can meet with the same sequence of properties. This period containing 32 elements with another set of three transitional elements and 15 rare-earth elements, is called a *very long period* or *monster period.* The rare-earth elements are all placed in one group.

Then comes a fragmentary period containing only 6 elements all of which are *radio-active.* It ends with Uranium, the element with the highest atomic weight known.

Those elements that fall in the first eight places of the long periods are stated to form the *even series*, while the last seven are distinguished as forming the *odd series.*

In this manner the elements are arranged in nine vertical *groups.* The first of these groups contains the so-called "inert gases". And as the system of numbering the groups of elements in the periodic arrangement has become familiarised by long use, this group containing the "inert gases" has been numbered Group O, and the systematic numbering of the other groups begins as usual. The last group, *viz.*, the Group VIII, contains the transitional elements that come between the even and odd series of the long periods.

In each of the remaining seven groups, the elements belonging to the even series of their respective long periods, are placed to the left, while those belonging to the odd series are arranged on the right-hand side of each vertical column. In this way the groups are divided into the sub-divisions A and B, in which the resemblance between the members is most pronounced. Thus, in Group II, although there are certain properties common to all the members there is a much closer similarity existing between the elements calcium, strontium and barium than between zinc and calcium, cadmium and barium. The elements in the two short periods have been placed in that sub-division with the members to which they exhibit the closer resemblance. Thus, in Group I, lithium and sodium are more allied to potassium, rubidium, and caesium, than to copper, silver and gold ; while in Group VII fluorine and chlorine are placed in the same family with bromine and iodine, with which they exhibit a close similarity.

Periodicity in the properties of the elements, when arranged in the Periodic Table is shown by the physical properties like melting point, boiling point, specific gravity, conductivity for heat and electricity etc., and is best illustrated by the atomic volume curve. Atomic volume of an element is $\frac{At.\ wt.}{Sp.\ gr.}$ for the element. When the values for atomic volumes are plotted against at. wts. of elements, with at. wts. as abscissæ and at. volumes as ordinates, a curve is obtained, which is distinctly periodic.

The periodicity in the chemical properties of the elements when arranged in the Periodic Table is seen by taking into consideration *valency* and *electro-chemical character* of the elements.

(*a*) *Valency.*—The elements of Group O have zero valency. The valencies of the elements towards hydrogen increase regularly from 1 to 4 while passing from Group I to Group IV and then diminish from 3 upto 1 from Group V to Group VII, as is evidenced from the formation of compounds like

LiH, CaH_2, $(BH_3)_2$ CH_4, NH_3, SH_2, FH,

The valencies towards oxygen, on the other hand, increase regularly from 1 to 8 as we pass on from Group I to Group VIII, as illustrated by formation of compounds like

Li_2O BeO B_2O_3 CO_2 N_2O_5 SO_3 Cl_2O_7 OsO_4.

(b) *Electro-chemical character.*—In Group I we find the elements which are highly *electro-positive.* Then gradually the electro-positive character diminishes until in Group IV we find elements like C, Si, etc. which are *electrically indifferent* Then from Group V upto VII the *electro-negative* character makes its appearance and the elements of Group VII are highly electro-negative. Then from highly electro-negative elements like F or Cl, the transition to the highly electro-positive elements like Na or K takes place through elements like Ne or A which have no valency and therefore of electrical character infinity. Hence a regular periodicity is exhibited in electro-chemical character, when we consider the elements as arranged in the Periodic Table.

Usefulness of the Periodic Table :—

The uses of the Periodic system are found

1. *In the classification of the elements* :—It is the best of all the methods of classifying the elements. It has rendered the study of about 90 elements into that of nine vertical groups.

2. *In correcting doubtful Atomic weights.*—One example will make this clear. The equivalent weight of Indium was found to be 38. Its at. wt. was taken as 2 × 38 = 76. In that case Indium is to be placed between Arsenic and Selenium. But there was no room for such an element there. Mendeleeff, judging from its properties, suggested that Indium should have an atomic weight 3 × 38 = 114 which would place it between Cadmium and Tin, where it fits very well. The subsequent determination of the atomic heat of Indium and thence its at. wt. corroborated this change and the correct at. wt. of Indium is taken as 114 and not 76.

3. *In the prediction of new elements.*—At the time when the

Periodic law was first formulated, there were three gaps in the system in the first long period, *viz.*, No. 4 in the even series (now occupied by Scandium), and Nos. 3 and 4 in the odd series (now filled by Gallium and Germanium). To the unknown elements which were destined to occupy those positions, Mendeleeff gave the names *eka-boron*, *eka-aluminium*, and *eka-silicon* and from the known properties of the neighbouring elements of the series and also of those situated nearest in the same family, he predicted some of the prominent properties that would probably be possessed by these elements. These predictions came out to be true when in 1875 Lecoq de Boisbaudran discovered Gallium tallying in properties with eka-aluminium. Discovery of Scandium (Nilson 1879) and Germanium (Winkler, 1886) whose properties were found to accord closely with those of eka-boron and eka-silicon respectively formed an additional demonstration of the truth of the Periodic law.

Defects of the Periodic classification :—

1. The position of Hydrogen is yet open to discussion. It is monovalent and so can be placed either in Group I with the alkali metals or in Group VII with the halogens. The only argument for placing Hydrogen with the alkali metals is that it is an electro-positive element like the alkali metals. Arguments in favour of placing Hydrogen in Group VII with the halogens are :—

(1) Like the first two members of the halogen family, *viz.*, F and Cl, it is a gas. (2) Like the halogens, its molecules are diatomic. (3) It may be replaced, atom for atom, from organic compounds, by the halogens. (4) Just as the metals form halides with the halogens, similarly alkali metals and the alkaline earths form definite hydrides with Hydrogen and in these hydries Hydrogen behaves as an electro-negative element. (5) If Hydrogen be placed in Group VII, the difference between the at. wts. of Hydrogen and its next congener Fluorine is ·18 which is the usual difference between the atomic wts. of two successive elements in the same group in the first two short periods ; but this sequence is broken, if it be placed in Group I. To avoid these difficulties Hydrogen has been placed at the head of the table in a separate series by itself.

2. In the case of some elements, the atomic weight sequence is broken : thus in three sets

(*a*) Argon (39·9) and Potassium (39·0)
(*b*) Cobalt (58·9) and Nickel (58·6)
(*c*) Tellurium (127·5) and Iodine (126·9)

Atomic wt. sequence is reversed on chemical grounds.

3. There are fifteen rare-earth elements for which appropriate places have not been found.

4. The periodic classification according to atomic weights overlooks certain chemical analogies. For example :

(*a*) Copper, Silver and Gold have very little analogies with Sodium, Potassium, etc. and yet they have been placed in the same group with the alkali metals. Similarly, Manganese has been placed in the same group with the Halogens.

(*b*) Copper and Mercury, Silver and Thallium, Barium and Lead, which appear to be chemically similar, are placed in separate groups.

Q. 3. *What are the most common ores from which silver is isolated ? Give a clear but concise account of the process involved in the separation of silver from its ores. Indicate the method for refining silver.*

A piece of silver jewellery is given to you ; how will you prepare pure silver from it ?

Ans. Silver is most commonly extracted from its sulphide and chloride ores and oftentimes from argentiferous galena, PbS. Important ores of silver are :—

(1) Argentite or Silver glance, Ag_2S
(2) Copper-silver glance or stromeyetrite, $(Cu, Ag)_2S$
(3) Ruby Silver or Pyrargyrite, $3Ag_2S, Sb_2S_3$
(4) Horn silver or Chlorargyrite, AgCl
(5) Proustite, $3Ag_2S, As_2S_3$.

Extraction of Silver :—

Siver may be extracted from its ores either by a dry process or by a wet process. In the dry process silver ores are smelted with lead ores or with metallic lead, when an alloy of lead and silver is produced. When the lead-silver alloy is rich in silver, lead is removed by the *cupellation process* described below : but when lead-silver alloy contains less than 1% of silver, it is subjected to a preliminary concentration process, either by Pattison's process or by Parke's process and then subjected to cupellation process.

Cupellation Process.—The alloy of lead and silver, rich in silver, is placed in an oval-shaped dish, made of bone-ash or marl, called the *cupel* or *test.* The cupel is then fixed on the bed of a reverberatory furnace, heated strongly and a blast of air is projected on the alloy.

Lead is oxidised to lead monoxide by the blast of air and the molten oxide of lead (litharge) overflows by the force of the blast into iron pots placed below. Silver escapes oxidation.

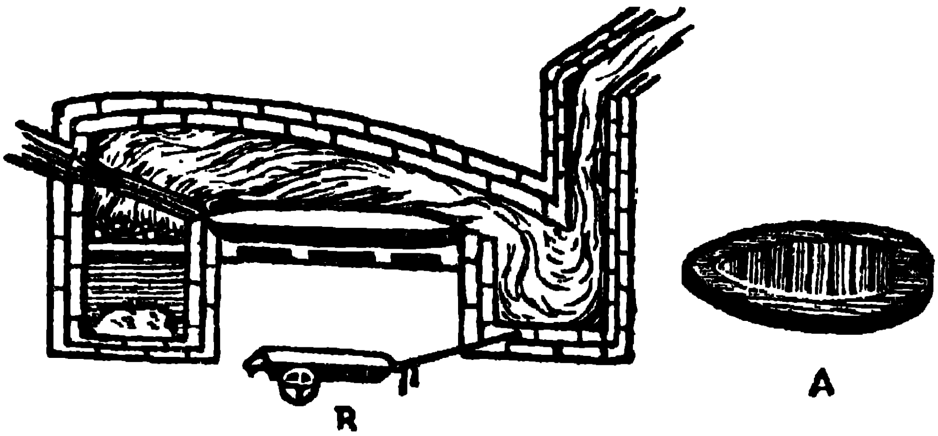


Fig 13.

Lead is completely oxidised and removed, and at the end the thin film of litharge, still left, is absorbed completely by the porous cupel. Then the bright surface of silver suddenly shows itself, the phenemenon being known as the *flashing of silver.* The metal so produced is removed.

When the lead-silver alloy contains less than 1% of silver, it is concentrated by Parkes' process, now mostly in use. It is based upon the facts (1) that molten zinc and molen lead are nearly immiscible and (2) that silver is much more soluble in zinc than in lead. Hence, when zinc is added in molten condition to molten argentiferous lead, most of the silver goes to form an alloy with zinc. This alloy floats on the surface of molten lead. This, on cooling, solidifies before lead begins to solidify. This solid alloy of zinc and silver is therefore readily skimmed off by perforated ladles. This zinc-silver alloy is then distilled from plumbago retorts, when zinc distils over, leaving behind silver alloyed with a little lead. This lead-silver alloy rich in silver is then cupelled as described above.

The action of zinc here is to extract silver from lead and alloy with the silver extracted forming a lighter and less fusible alloy than the alloy of lead and silver. From this zinc-silver alloy, zinc can be easily separated by the process of distillation, zinc being the most volatile metal of the three : zinc, silver and lead.

The wet process for extraction of silver is by the cyanide process, which is now in most use. In this process, the finely crushed ore of silver is treated with a 0·7% solution of sodium cyanide in water. The mass is then well agitated by a current of air. Sodium cyanide dissolves silver sulphide, giving soluble sodium argento-cyanide, $NaAg(CN)_2$. Na_2S, also formed during the reaction, tries to stop the reaction ; but it is oxidised by the current of air to sodium thiosulphate, $Na_2S_2O_3$.

$$Ag_2S + 4NaCN = 2NaAg(CN)_2 + Na_2S.$$
$$2Na_2S + 2O_2 + H_2O = Na_2S_2O_3 + 2NaOH.$$

The silver is then precipitated from the filtered solution by the addition of scrap zinc or aluminium powder.

$$2NaAg(CN)_2 + Zn = 2Ag + Na_2Zn(CN)_4.$$

Method for refining silver :—

Silver can be made in a state of great purity. It is precipitated from a solution of pure silver nitrate with grape sugar. The product is next fused in a boat made of pure quicklime. The fusion is to be carried out in hydrogen or in a vacuum, for molten silver absorbs considerable quantities of oxygen, which are mostly given out on cooling. By this process Richard and his co-workers were able to prepare 99·999 per cent. pure silver.

Silver can also be refined by an electrolytic process. The electrolyte is a weak solution of silver nitrate (5 to 10%) containing 1% free nitric acid, taken in a cell. The cathode is a thin plate of pure silver and the anode is a thick slab of impure silver to be refined, both dipped in the solution of $AgNO_3$ containing HNO_3 as mentioned before. Electric current is then passed through the solution in the cell at an E.M.F. of about 1·5 volts. Silver is deposited on the cathode and copper, gold etc., passed into solution in the bath or are deposited at the bottom.

Copper in the bath should not be allowed to accumulate beyond 5%. Deposited silver is scraped off, well-washed, melted in an atmosphere of hydrogen and cast into slabs. This silver is 99·9 per cent. pure.

From a piece of silver jewellery, containing Cu and other metals alloyed with silver, pure silver can be obtained by the following operations :—First of all it is to be cut to small pieces and dissolved in strong nitric acid and the solution is evaporated to dryness on a water bath. The residue is then dissolved again in distilled water. The aqueous solution is then taken in a beaker and dilute hydrochloric acid is added to it till percipitation is complete. By this means silver chloride is obtained as a precipitate. The solution, with AgCl as precipitate, is heated to boiling, filtered and the precipitate of AgCl is well washed with hot water. AgCl is next thoroughly dried and fused with pure Na_2CO_3 inside a crucible made of pure lime when a button of pure silver is obtained. $Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O$; $AgNO_3 + HCl = AgCl + HNO_3$.

$$4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + 2CO_2 + O_2.$$

Q. 4. *A mixture is suspected to contain salts of copper, iron and aluminium. How do you propose to separate the metals and isolate them in the form of charactertstic salt in each case ?*

Explain clearly the principle involved.

Ans. The mixture containing the salts of copper, iron and aluminium is dissolved in water or in dilute hydrochloric acid. Since these are all salts, most probably they will dissolve in HCl.

The HCl solution is heated to boiling and H_2S gas is passed into it till the precipitation is complete. Black precipitate of CuS from copper salt present in solution is produced. Iron and aluminium remain in solution, for their sulphides are soluble in acids.

The black ppt. of CuS is separated by filtration, and the filtrate contains all the iron and aluminium in solution.

Thus copper is obtained as copper sulphide, a salt of copper.

The filtrate is boiled to remove all H_2S and then a few drops of conc. HNO_3 added to convert ferrous salt to the ferric state. About 1 gram of NH_4Cl is then added to the solution and the hot solution is treated with NH_4OH till the solution smells strongly of ammonia.

Brown precipitate consisting of ferric hydroxide and aluminium hydroxide is now obtained. The solution containing the precipitate is then filtered and washed with hot water. The precipitate is then transferred to a beaker, dissolved in the least quantity of dil. HCl, the acid neutralised with NaOH solution and then made alkaline with addition of 5 c.c. more of NaOH solution. Then about 1 gram of Na_2O_2 is added to it with stirring. The mixture is boiled for 2 or 3 minutes and then sufficiently diluted and filtered. The residue is ferric hydroxide and aluminium hydroxide passes in the filtrate as sodium aluminate $NaAlO_2$.

The residue of ferric hydroxide after thorough washing is dissolved in dilute H_2SO_4 and the solution concentrated to crystallisation, when crystals of ferric sulphate, $Fe_2(SO_4)_3$, separate out.

From the filtrate, aluminium hydroxide is precipitated by boiling with NH_4Cl. This $Al(OH)_3$ is filtered and washed thoroughly, and then dissolved in dil. H_2SO_4 and the solution so obtained is evaporated to crystallisation. Thus crystals of aluminium sulphate, $Al_2(SO_4)_3, 18H_2O$, are obtained.

The principles involved herein are the following :—Of the three metals mentioned to be present, only copper can be precipitated as sulphide from HCl solution, but neither iron nor aluminium. So copper can be readily separated as CuS by passing H_2S through HCl solution of the salts of the metals mentioned.

Iron and aluminium can both be precipitated as their hydroxides by NH_4OH in presence of ammonium salts, after separation of copper and removal of H_2S by boiling, iron being converted fully to the ferric state. Hence the use of a few drops of HNO_3 after removal of H_2S by boiling, for conversion of any ferrous salt present or formed due to the reducing action of H_2S to the ferric state.

The separation of iron from aluminium depends upon the ready solubility of aluminium hydroxide in Na_2O_2 and insolubility of ferric hydroxide in the same. Aluminium passes into solution as sodium aluminate, $NaAlO_2$.

Q. 5. *What are the ingredients that are necessary for the preparation of the compounds ;—(a) Bleaching powder, (b) Lead peroxide, (c) Orthophosphoric acid and (d) Ferrous ammonium sulphate.*

Mention the experimental conditions necessary to bring about the reaction. Write clearly the equations to represent the changes. State the uses of the above substances, if any.

Ans. (*a*) For the preparation of bleaching power the ingredients necessary are dry slaked lime, $Ca(OH)_2$ and chlorine gas free from HCl and CO_2.

It is prepared by spreading dry slaked lime over the floor of a closed lead chamber provided with glass doors and widows and the lime is raked into furrows to expose a large surface. Somewhat diluted chlorine free from HCl and CO_2 is led in. Chlorine is at first rapidly absorbed, but the reaction afterwards slows down. The lime is raked up from time to time. The excess of chlorine which is left unabsorbed is removed by dusting in lime into the room by a special fan arrangement. The temperature is maintained at 35—40°C.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Uses.—Bleaching powder is used for bleaching purposes and also as a disinfectant.

(*b*) *Lead peroxide.*—Red lead, Pb_3O_4, and concentrated nitric acid, HNO_3, are the ingredients necessary for its preparation.

Cold conc. HNO_3 is added to red lead and the mixture thoroughly stirred. The solution is then diluted, filtered and lead peroxide. PbO_2, formed is washed and dried.

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O + PbO_2.$$

Uses.—It is used in the manufacture of matches, in the storage battery and as an oxidising agent.

(*c*) *Orthophosphoric acid*, H_3PO_4.

Bone-ash and dilute sulphuric acid are the ingredients necessary for its preparation.

Bone-ash is digested with requisite amount of dilute sulphuric acid for the several hours. The precipitated calcium sulphate is filtered off and the filtrate concentrated to a syrupy consistency.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

This gives only 80% orthophosphoric acid. The best way to get the pure acid is to start with red phosphorus and conc. HNO_3. Red phosphorus is boiled with conc. HNO_3 in a flask provided with an upright condenser. When all the phosphorus has gone into solution and the evolution of the red fumes has ceased, a little of the solution is taken out, diluted and treated with silver nitrate solution. If there be any black precipitate, a little more conc. HNO_3 is added and boiling continued, so that phosphorous acid, H_3PO_3, formed may be oxidised to phosphoric acid, H_3PO_4.

$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

The liquid is then poured in a procelain basin, and evaporated over a small flame till the temperature rises just to 180°C. The basin containing the hot liquid is then placed in a vaccum desiccator over concentrated H_2SO_4 and the desiccator is cooled in a freezing mixture of ice and salt, when crystals of orthophosphoric acid slowly separate. These crystals, which are deliquesent, have a melting point of 38·6°C.

Uses.—Orthophosphoric acid is used in the preparation of lemonades, as a preservative of hydrogen peroxide, and sometimes for preparation of phosphates.

(*d*) *Ferrous ammonium sulphate* or Mohr's salt $(NH_4)_2SO_4,FeSO_4,6H_2O$. Ingredients necessary for its preparation are ferrous sulphate and ammonium sulphate. Green vitriol, $FeSO_4 7H_2O$, crystals and ammonium sulphate are taken in equimolecular proportion and dissolved in warm water to produce a saturated solution. The solutions are then filtered and mixed together. On cooling, crystals of ferrous ammonium sulphate separate out. These are filtered and dried in a vacuum desiccator over conc. H_2SO_4.

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O = FeSO_4, (NH_4)_2SO_4, 6H_2O.$$

Uses.—This salt is used in the laboratory in volumetric analysis, since it is known to contain iron to the extent of one-seventh of its molecular weight.

Q. 6. *How do an acid, a base and an acid salt behave? What are your reasons for calling hydrochloric, sulphuric and phosphoric acids, monobasic, dibasic and tribasic respectively? What method would you adopt for preparing an acid salt of one of these acids?*

Ans. *Acid.*—An acid solution is capable of turning blue litmus red and methyl orange pink. When added to a carbonate, effervescence will occur. It will react with a base producing salt and water. According to ionic theory, an acid will give hydrogen ions in water solution.

Base.—When in solution a base is capable turning red litums blue, methyl orange yellow and phenophthalein pink. It will react with an acid producing salt and water. According to ionic theory. a base, when present in water solution, gives hydroxyl ions.

Acid salt.—Soluble *acid salts* usually turn blue litmus solution red. These are capable of reacting with further quantities of base, producing a normal salt and water. These will also effervesce usually with a carbonate.

Hydrochloric acid is monobasic, because it contains one atom of replaceable hydrogen. It is found to be capable of giving rise only to normal salts. no acid salt being known.

$$HCl + NaOH = NaCl + H_2O.$$

Sulphuric acid is dibasic because it contains two atoms of replaceable hydrogen. Hydrogen present in sulphuric acid can be replaced in stages. By adding half the quantity of caustic soda required to neutralise fully the acid, and then crystallising, sodium bisulphate is produced. Only one acid salt, *viz.*, this acid sodium sulphate, is known in the case of this acid. When exact quantity of caustic soda required to neutralise sulphuric acid is added to the acid and the mixture crystallised, normal sodium sulphate is obtained.

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O.$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

Phosphoric acid is tribasic, for it contains three atoms of replaceable hydrogen. By successive addition of NaOH in stages, we can get two acid salts, NaH_2PO_4 and Na_2HPO_4 and one normal salt, Na_3PO_4. Thus it is proved that phosphoric acid is tribasic in character.

Preparation of acid salt.—A certain quantity of sulphuric acid is taken in a beaker and this quantity is divided exactly into two equal halves and taken in two different beakers. Sulphuric acid contained in one beaker is exactly neutralised with caustic soda solution by using litmus as indicator. To this neutralised solution the other half of sulphuric acid is added and the mixed solution is then evaporatod to dryness, when crystals of sodium hydrogen sulphate, $NaHSO_4$, an acid salt, are obtained,

Q. 7. *To what class of substances, oxidising or reducing agents, do the following belong : sulphur dioxide, nitric acid, carbon monoxide and chlorine ?*

Describe an experiment in each case to justify your classification and also give arguments in favour of your conclusion.

Ans. *Sulphur dioxide.*—Usually a strong reducing agent.

Experiment.—Sulphur dioxide is passed into ferric chloride solution acidified with hydrochloric acid. The solution changes in colour from yellow to nearly colourless (slightly greenish),

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

When ammonium thiocyanate is added to ferric chloride solution originally taken, a blood-red coloration is produced. But the colourless solution obtained by treatment of ferric chloride solution with SO_2 when treated with ammonium thiocyanate, gives no blood-red coloration, showing thereby that no ferric ion is present in the solution. But an addition of a solution of potassium ferrocyanide to the colourless solution produced by treatment witb SO_2, causes a deep blue ppt. to be formed. This shows the presence of ferrous ion in the solution. At the same time, if we add $BaCl_2$ solution to the colourless solution obtained by treating with SO_2, a white precipitate, insoluble in HCl, is obtained. This proves the presence of sulphate ion in the solution.

Thus, here ferric chloride is changed into ferrous chloride with the reduction in the proportion of electro-negative element chlorine in the compound ferric chloride, whereas SO_2 is oxidised into SO_3 which with water gives sulphuric acid with an increase in the proportion of electro-negative element,

Hence sulphur dioxide is a reducing agent.

But sometimes sulphur dioxide acts as an oxidising agent.

Experiment.—SO_2 is passed into a solution of H_2S in water. Sulphur is precipitated as is observed from the milkiness of the solution and by burning a little of the solid separating in the reaction when smell of SO_2 is perceived.

$$2H_2S + SO_2 = 2H_2O + 3S.$$

Here hydrogen, an electro-positive element, is removed from the compound sulphuretted hydrogen and so it is oxidised, whereas sulphur dioxide loses oxygen, an electro-negative element and so it is reduced.

Nitric acid is a strong oxidising agent.

Experiment.—Some pure $FeSO_4$ solution is dissolved in *air-free* water. A little of it is taken in a test tube and potassium ferrocyanide solution is added to it. No blue precipitate is formed. Then the original ferrous sulphate solution is boiled with conc. HNO_3 and sulphuric acid. The solution is cooled and then treated with potassium ferrocyanide solution. A deep-blue precipitate is obtained. This proves the presence of ferric ion in the solution. Thus ferrous sulphate is oxidised to ferric sulphate since there is an increase in the proportion of electro-negative part in the compound ferrous sulphate. At the same time nitric acid is reduced to nitric oxide as is observed during the addition of nitric acid to ferrous sulphate solution which turns deep brown due to the absorption of NO produced by unchanged ferrous sulphate with the formation of the compound $FeSO_4, NO$.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

Therefore, *nitric acid* is a strong oxidising agent.

Carbon monoxide is a strong reducing agent.

Experiment.—Black copper oxide is heated in a bulb tube and carbon monoxide is passed over it. The gas coming out of the tube is passed into lime water when the lime water is found to turn milky, proving thereby that carbon dioxide has been produced. At the same time black oxide of copper is changed into red metallic copper. Thus, copper oxide is reduced to metallic copper by loss of oxygen, an electro-negative element, and carbon monoxide is oxidised to carbon dioxide by addition of oxygen, an electro-negative element.

$$CuO + CO = Cu + CO_2.$$

Therefore, carbon monoxide is a reducing agent.

Chlorine is a strong oxidising agent.

Experiment.—Chlorine is passed into a solution of sulphur dioxide in water. The greenish-yellow colour of chlorine disappears. The solution of sulphur dioxide in water produces a white precipitate with $BaCl_2$ solution, but the white ppt. dissolves in HCl. After passing chlorine through the solution of SO_2 in water. $BaCl_2$ sol. produces a white ppt. insoluble in HCl proving thereby that sulphate ions are present in the solution. Thus SO_2 is oxidised to SO_3 (which with water produces sulphuric acid) by addition of oxygen, an electro-negative element. At the same time $AgNO_3$ sol. gives a curdy white ppt. insoluble in HNO_3 but soluble in NH_4OH, proving thereby that chloride ion is present in the solution. Chlorine is reduced to HCl by addition of hydrogen, an electro-positive element.

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

Hence *chlorine* is a strong oxidising agent.

Q. 8. *The gaseous product of a lime kiln was led into a solution of sodium hydroxide until no further quantity of the gas was absorbed. The solid product thus obtained was heated at a rather elevated temperature for a sufficiently long time and then it was crystallised from water. The product was next treated separately with a solution of bleaching powder, iodine and hydrogen chloride. What were the products finally obtained ?*

Describe the changes that occurred, illustrating your answer with equations.

Ans. The lime kiln gas is carbon dioxide, produced therein by the decomposition of limestone, $CaCO_3$.

$$CaCO_3 = CaO + CO_2.$$

When carbon dioxide, thus obtained, is led into a solution of sodium hydroxide, CO_2 is absorbed by NaOH with the formation of sodium carbonate at the first instance, but on passing

CO_2 continuously to saturation, sodium bicarbonate is produced.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

The solid product that separates out is sodium bicarbonate. When this sodium bicarbonate is heated at a rather elevated temperature for a sufficiently long time it is converted into sodium carbonate with evolution of carbon dioxide and water in the form of steam.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

When this sodium carbonate is crystallised from water, we get crystals of sodium carbonate decahydrate, $Na_2CO_3, 10H_2O$.

(*a*) When this sodium carbonate decahydrate is treated with a solution bleaching powder, calcium carbonate is precipitated, and sodium chloride and sodium hypochlorite are formed in solution.

$$Ca(OCl)\,Cl + Na_2CO_3 = CaCO_3 + NaCl + NaOCl.$$

(*b*) A solution of iodine contains hydriodic acid and hypo-iodous acid. Hydriodic acid gives iodide with sodium carbonate and hypo-iodous acid produces sodium hypo-iodite. But alkali hypo-iodite is hydrolysed by water into hypo-iodous acid even in presence of alkali. Thus, after addition of a solution of iodine to sodium carbonate decahydrate, the solution contains sodium iodide and hypo-iodous acid.

$$I_2 + H_2O \rightleftharpoons HI + HOI$$
$$Na_2CO_3 + 2HI = 2NaI + CO_2 + H_2O$$
$$Na_2CO_3 + 2HOI + 2NaOI + H_2O + CO_2$$
$$NaOI + H_2O \rightleftharpoons NaOH + HOI.$$

Thus at the end we have in the solution sodium iodide, hypo-iodous acid, a little sodium hypo-iodite and caustic soda.

(*c*) When a solution of hydrogen chloride is added to sodium carbonate, carbon dioxide is evolved and sodium chloride is formed along with water. The solution effervesces due to rapid evolution of carbon dioxide.

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$

1943

FIRST PAPER

Q. 1. *Explain and illustrate what you understand by electrolysis'.*

State Faraday's laws of electrolysis.

How would you proceed to determine the equivalont weight of copper by electrolysis of a copper sulphate solution ?

Ans. Electrolysis is the process in which an eletrolyte (generally aqueous solutions of acids, bases, or salts or fused alkalies or fused salts) is decomposed by the passage of an electric current through it, so that the products of decomposition are obtained at different electrodes placed inside the solution of the electrolyte or in the fused electrolyte.

Indeed, the aqueous solution of the electrolyte or the fused electrolyte is not really undergoing decomposition by the passage of the current but dissociated ions are already present in electrolytes under the conditions mentioned. The ions carrying electric charges are discharged at the oppositely charged electrodes and after neutralisation of their charges the discharged ions collect as ordinary molecules at the respective electrodes, the positively charged ions at the cathode and negatively charged ions at the anode.

Ans. *Faraday's laws of electrolysis* : These are two in number.

(1) The mass of an ion liberated during electrolysis is directly proportional to the strength of the current and to the time during which the current flows, *i.e.*, to the quantity of electricity flowing through the circuit.

Thus, if W be the mass in grams of an ion liberated, C the strength of the current in ampere and t the time in second during which the current flows, $W \propto Ct$, or $W = ZCt$, where Z is a constant. Now when $C = 1$ amp. and $t = 1$ sec., then $W = Z =$ mass of ion liberated by unit quantity of electricity. This quantity Z is called the *electro-chemical* equivalent of the substance.

(2) When the same quantity of electricity is passed through different electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.

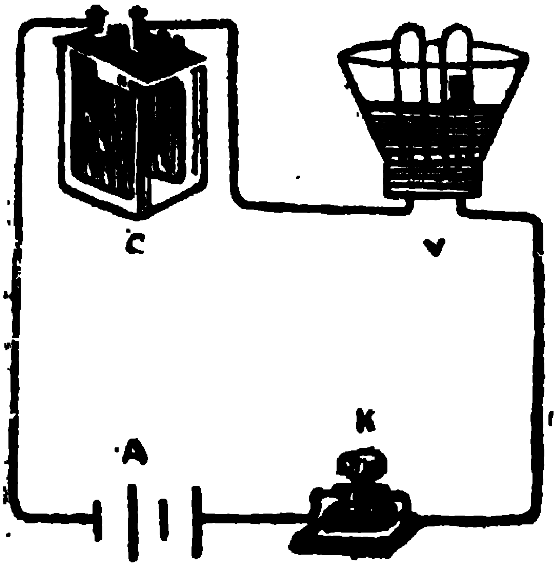


Fig. 14.

A copper voltameter, containing *pure* copper sulphate solution acidified with dil. H_2SO_4 and a water voltameter containing acidulated water are joined in series with two storage cells and a plug key in the circuit (Fig. 14).

The plug is taken out. The copper cathode of the copper voltameter is then taken out and cleansed, first by rubbing it with sand paper, then washing with very dilute HNO_3, next with tap water and finally with distilled water and the copper cathode is then dried in a hot airbath. The clean, dry copper cathode is then weighed in a chemical balance carefully. Two gas measuring tubes are filled with acidulated water and is inverted over the two electrodes of the water voltameter. The weighed copper cathode is then replaced and the plug is then put in. The same current then passes simultaneously through the two voltameters. The current is allowed to pass for about half an hour. The copper cathode is then taken out and the deposit is examined which is found to be a smooth, salmon-coloured uniform deposit of copper in case the experiment is properly performed. The copper cathode is next washed with distilled water very carefully and then dried by gently warming it by holding it above a Bunsen flame. Care must be taken to avoid oxidation of the surface of the deposited copper. The cathode is then carefully weighed. The gas measuring tube, placed over the cathode of the water voltameter in which hydrogen has collected, is removed from over the cathode after closing it with the thumb and immersed in a tall jar of water. The volume of hydrogen collected is measured after adjusting the levels of water inside and outside the tube to the same height. The temperature of water in the tall jar is noted. This is also the temperature of hydrogen. The barometer reading is also taken. This volume of hydrogen is then corrected to N.T.P. allowing for the aqueous tension. Let V. c.c. be the volume of hydrogen at N.T.P.

The weight of hydrogen, liberated during the time a certain weight, say W grams, of copper (as obtained from the difference in weighings of the copper cathode at the beginning and end of the experiment) is collected is $V \times \cdot 00009$ grams. Then, the equivalent weight of copper is that weight of it which is liberated during the time 1 gram of hydrogen is collected by electrolysis, as follows from the 2nd law of electrolysis as stated by Faraday.

Therefore, Equivalent weight of $\text{Cu} = \dfrac{W}{V \times \cdot 00009}$.

Q. 2. *Describe* two *methods for the preparation of hydrogen from a solution of caustic soda.*

Under what conditions does hydrogen act best as a reducing agent ?

How would you employ hydrogen for reducing :—

(a) Copper oxide, (b) a solution of ferric chloride ? Prove that a molecule of hydrogen consists at least of two atoms.

Ans. (*i*) Hydrogen can be obtained from caustic soda by boiling a strong solution of caustic soda with powdered zinc or aluminium in a flask provided with a cork and a delivery tube, the hydrogen evolved being collected by displacement of water.

$$Zn + 2NaOH = Na_2ZnO_2 + H_2$$

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

(*ii*) Hydrogen can also be obtained from caustic soda by the electrolysis of fused caustic soda in an iron vessel set in a suitable brick-work, the *cathode* being an iron rod inserted through the bottom and kept in position by allowing the caustic soda in the lower narrow part of the vessel to solidify and the *anode* a cylinder of nickel. Hydrogen, along with sodium, is liberated at the cathode. Hydrogen collects in an iron vessels, suspended from the top of the vessel, open at the bottom but closed with a lid at the top. Hydrogen escapes from the lid and is collected.

Hydrogen acts as a reducing agent either in the *nascent state*, i.e., if the hydrogen be allowed to be evolved in the solution which is to be reduced, or when the substance to be reduced is strongly heated before hydrogen gas is passed over it.

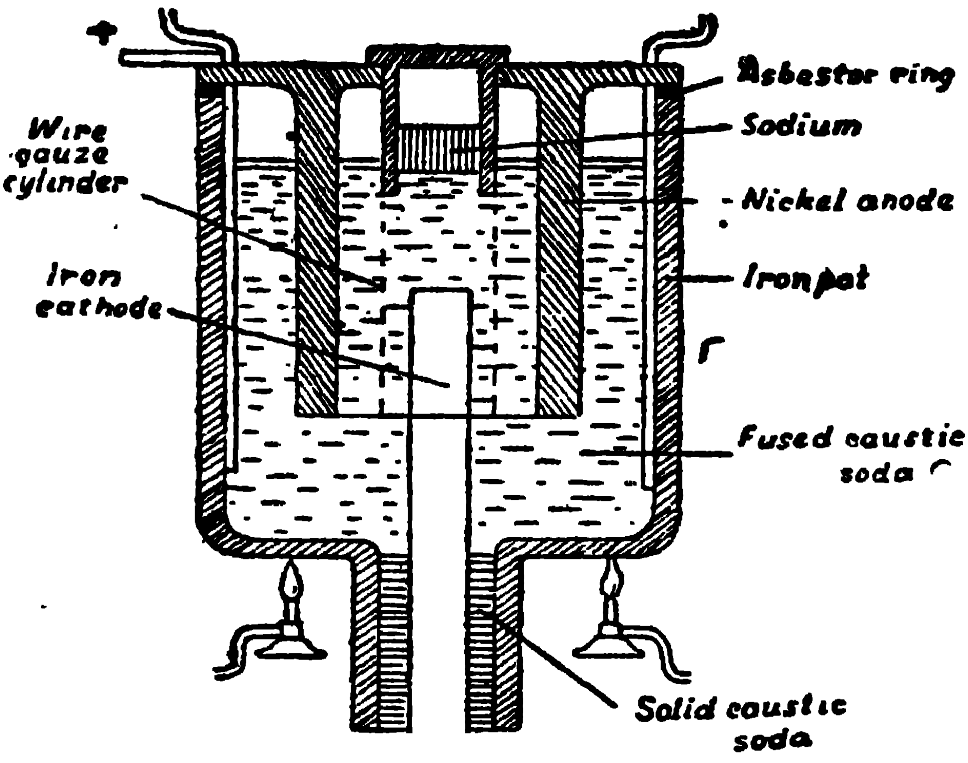


Fig. 15.

(*a*) Copper oxide is taken in a bulb tube and heated to red heat when all the air from the bulb tube is displaced by hydrogen. The current of hydrogen is continued for a certain length of time when red metallic copper is produced. The flame is removed and the tube is cooled in the atmosphere of hydrogen.

$$CuO + H_2 = Cu + H_2O.$$

(*b*) The solution of ferric chloride is taken in a beaker and HCl is added to it. Granulated zinc is dropped into it. Hydrogen is liberated in the nascent state and this nascent hydrogen reduces ferric chloride, as is evidenced from the change of colour of the solution from yellow to colourless (faintly greenish).

$$Zn + 2HCl = ZnCl_2 + 2H$$
$$2FeCl_3 + 2H = 2FeCl_2 + 2HCl.$$

From actual experiment we know that 1 vol. of hydrogen combines with 1 vol. of chlorine to produce 2 vols. of hydrochlorine acid gas.

Let *n* be the number of molecules present in 1 vol. of hydrogen.

Then, from Avogadro's hypothesis, we have *n* molecules of hydrogen combining with *n* molecules of chlorine give rise to *2n* molecules of hydrochloric acid gas ;

Or, 1 molecule of hydrogen combining with one molecule of chlorine produces 2 molecules of hydrochloric acid gas. Now, since hydrochloric acid gas is a compound of hydrogen and chlorine only, each molecule of hydrochloric acid gas must contain *at least* 1 atom of hydrogen and 1 atom of chlorine, since atoms are indivisible. Therefore, 2 molecules of hydrochloric acid gas must contain *at least* 2 atoms of hydrogen and 2 atoms of chlorine. Now, these 2 atoms of hydrogen in 2 molecules of hydrochloric acid gas must have come from 1 molecule of hydrogen. Thus it is proved that a molecule of hydrogen consists *at least* of 2 atoms of hydrogen.

Q. 3. *Describe how would you determine the composition of carbon dioxide by weight and by volume. Deduce its molecular formula from the results.*

How would you account for its presence in the atmosphere almost in constant quantities ? What function does it play in the growth of plants ?

Ans. Composition of carbon dioxide by weight :—

A porcelain boat is taken and accurately weighed. Some pure sugar charcoal is taken in the porcelain boat and the boat with the sugar charcoal is weighed again. The boat is next introduced into a hard glass tube, about $\frac{3}{4}$ part in which is filled up with coarse copper oxide (CuO). The hard glass tube is then placed in a furnace. The end of the tube nearer the porcelain boat is connected, through *U*-tubes, *A* and *B*, *A* being filled with KOH and *B* with glass beads and concentrated H_2SO_4, to an apparatus for supplying pure dry oxygen. The other end of the hard glass tube is joined with a potash bulb *C* containing a strong solution of KOH and a $CaCl_2$-tube *D*. The potash bulb together with the $CaCl_2$-tube is weighed carefully at the beginning of the experiment.

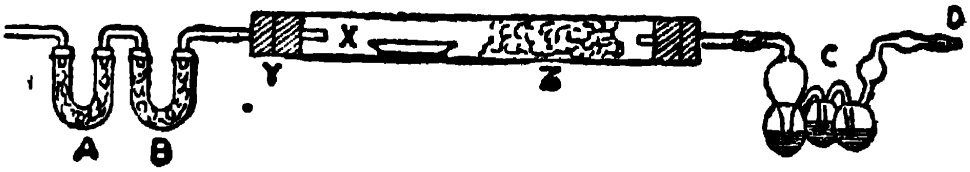


Fig. 16.

A slow current of pure and dry oxygen, freed from CO_2 bubbling through KOH and dried by passing through conc. H_2SO_4, is passed through the apparatus. The apparatus is fitted in such a fashion that it is airtight. The potash bulb with the $CaCl_2$-tube is then fitted at the other end. The hard glass tube is then heated gradually, at first the CuO portion being heated and the portion of the tube containing the boat being heated last. Sugar charcoal, taken in the boat, burns to carbon dioxide which passes on and is absorbed in the potash bulb. Any carbon monoxide that is produced due to incomplete combustion of sugar charcoal is oxidised into carbon dioxide by red-hot copper oxide and this carbon dioxide is also absorbed in the potash bulb. Any moisture that is driven out of the potash bulb by the current of oxygen is absorbed by the $CaCl_2$-tube *D*. After the combustion of sugar charcoal is complete and bubbles are seen not to be absorbed by KOH bulb, the heating is discontinued and the tube is cooled with tha current of oxygen passing on. This oxygen current sweeps out all the carbon dioxide formed and helps to re-oxidise metallic copper formed by the reduction of CuO by any CO formed. The porcelain boat is next taken out and if any ash be found to be left behind, the boat with the ash is weighed again. The difference between the second and the third weighings of the boat gives the amount of carbon burnt to carbon dioxide. The potash bulb with the $CaCl_2$-tube is then detached and weighed carefully. The difference between the first and the second weighings of the potash bulb with $CaCl_2$-tube gives the weight of carbon dioxide formed.

Molecular formula of carbon dioxide from the determination of composition of carbon dioxide by weight ;—

Let the weight of porcelain boat $= w_1$

" " " + sugar charcoal $= w_2$

" " " + ash $= w_3$

Wt. of KOH—bulb + $CaCl_2$ tube *before* the experiment $= w_4$
" " " " *after* " $= w_5$
Then the wt. of charcoal burnt out $= w_2 - w_3$
" " carbon dioxide formed $= w_5 - w_4$

Hence the weight of oxygen combining with $(w_2 - w_3)$ parts by weight of carbon $= (w_5 - w_4) - (w_2 - w_3)$.

If the experiment be carefully performed, it will be found that

$$\frac{\text{Wt. of carbon in carbon dioxide}}{\text{Wt. of oxygen in carbon dioxide}}$$

$$= \frac{w_2 - w_3}{(w_5 - w_4) - (w_2 - w_3)} = \frac{3}{8}.$$

Hence, from the experiment it is known that 8 parts by weight of oxygen combine with 3 parts by wt. of carbon to form carbon dioxide. Now, the density of carbon dioxide as found by experiment is 22. Therefore, the molecular weight of carbon dioxide is 44. Now, in 44 parts of carbon dioxide the amount of carbon present $= \frac{3}{11} \times 44 = 12$ and the amount of oxygen present $= \frac{8}{11} \times 44 = 32$. Now, 12 is the atomic weight of carbon and can stand for only one atom of carbon ; also 16 is the atomic weight of oxygen and therefore 32 can stand for 2 atoms of oxygen.

Hence the formula for carbon dioxide is CO_2.

Composition of carbon dioxide by volume :—

A *U*-shaped eudiometer tube, open at one end and provided with a bulb at the other, as shown in the adjoining figure, is taken. There is also a stop-cock near the bottom. The bulb is fitted with an air-tight glass-stopper having two stout copper wires, one of which carries a copper spoon, fitted to it. The spoon and the other wire are connected by a very fine platinum spiral.

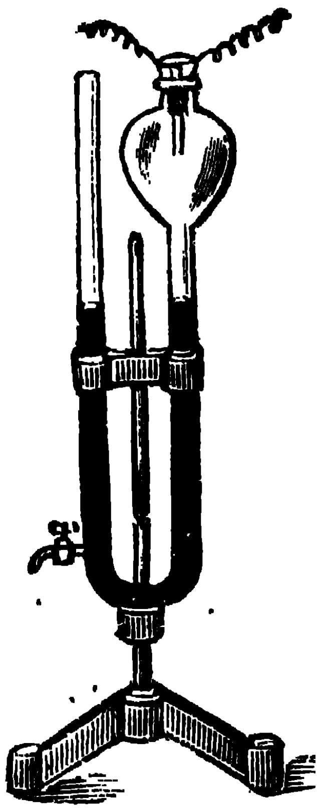


Fig. 17.

A piece of pure charcoal is taken on the spoon and the *U*-tube is filled completely with mercury. Pure dry oxygen is introduced in the *U*-tube by displacement of mercury in the limb fitted with the bulb. The stopper carrying the spoon containing pure charcoal is then replaced. The mercury level is then adjusted to the same height in both the limbs. The volume of oxygen is then noted. The two copper wires are then connected with the two terminals of a battery and electric current is passed through the Pt-wire. The Pt-wire becomes red-hot and ignites the charcoal. Carbon dioxide is produced and oxygen is used up. At first the mercury is depressed in the limb carrying the bulb owing to the thermal expansion of the volume of the gas. When the reaction is over, the apparatus is allowed to cool. Mercury is found to stand exactly at the same level in both the limbs as before. Thus, the volume of carbon dioxide produced is exactly the same as the volume of oxygen used up.

Hence carbon dioxide contains its own volume of oxygen.

Molecular formula of carbon dioxide from the determination of the composition of carbon dioxide by volume :—

From the experiment, we know that 1 vol. of carbon dioxide contains 1 vol. of oxygen. Let *n* be the number of molecules present in 1 vol. of carbon dioxide. Then, by Avogadro's hypothesis, *n* mols. of carbon dioxide contain *n* mols. of oxygen or 1 mol. of carbon dioxide contains 1 mol. of oxygen, or two atoms of oxygen, since oxygen molecule is diatomic (deduction from Avogadro's hypothesis).

Therefore, the formula of carbon dioxide is C_xO_2, where x is an integer.

Now, the density of carbon dioxide is 22 (experimental). Therefore the molecular weight of carbon dioxide is $2 \times 22 = 44$.

Now, 12 is the atomic weight of C and 16 is the atomic weight of oxygen.

Therefore, $12x + 32 = 44$,
whence $x = 1$.

Hence, the molecular formula for carbon dioxide is CO_2.

Carbon dioxide is produced by the combustion of fuel and during exhalations of animals. Carbon dioxide also comes out from lime-kilns and also from breweries. Thus, gradually the amount of CO_2 in air tries to go on increasing. Now, if there would have been no opposing reaction, some day all the oxygen would have been used up and CO_2 would have filled the whole atmosphere. But actually *three operations*, acting in opposite directions to the above, keep the amount of CO_2 in the atmosphere almost in constant quantities. (1) Plants have to depend for supply of carbon on the CO_2 of the air. Plants build up their tissues from CO_2 of the air by the following operations :—

Through the agency of the chlorophyll, or the green colouring matter of the plants, in presence of sunlight, the plants are capable of assimilating carbon from atmospheric carbon dioxide. Carbon dioxide is split off into carbon and oxygen ; oxygen escapes to air and carbon reacts with moisture forming at first formaldehyde : $C + H_2O = CH_2O$. Formaldehyde then polymerises into carbohydrates or sugar in which form it is assimilated by plants to build up their bodies. $6CH_2O = C_6H_{12}O_6$. Plants thus return to air oxygen which is lost by air during respiration of animals, combustion, etc.

(2) CO_2 is soluble in water to a moderate extent. A portion of CO_2 of air is dissolved out and removed by rain, river-water and other surface waters.

(3) A little quantity of CO_2 is also utilised in the weathering of rocks.

The above operations, occurring in nature, restore equilibrium in the composition of air and so CO_2 is present in air in almost constant quantity.

Q. 4. *What is rusting ? Explain the statement "rusting is a kind of slow combustion".*

A weighed quantity of iron filings was placed in a large glass flask of 5 litres capacity filled with air at N.T.P. After *moistening the iron filings with water the flask was closed air-tight by a stopper. On opening the flask after several months, the iron filings, when dried and weighed again, were found to gain 1·0714 gm. in weight. Calculate the change that was produced in the composition of air inside the flask at the time when it was opened. You must assume that air normally contains 20 per cent. oxygen and 80 per cent. nitrogen by volume. The presence of carbon-dioxide, water vapour, etc., may be ignored.*

Ans. *Rusting* is the process in which a piece of iron exposed to moist air is covered with a loose, non-coherent, easily detachable, brown coating called rust. According to Partington, rust is hydrated ferric oxide of the composition $2Fe_2O_3$, $3H_2O$. Other chemists, however, think that the composition of rust is not so simple. The composition of rust depends upon its age and hydrated ferric oxide predominates in the long run.

Rusting of iron takes place due to the combination of iron with the oxygen of air. Now combustion has been defined as any chemical reaction accompanied by the evolution of heat and sometimes light. For a long time the usual belief was that the phenomenon of combustion takes place in the presence of oxygen and so combustion was considered as rapid oxidation. Now it has been shown that combustion can take place in chlorine, bromine, etc., *e.g.*, Sb powder ignites and burns in chlorine gas. In a wider sense combination with any electro-negative element is oxidation. Hence in all cases combustion always involves oxidation. Phosphorus, when exposed to air, spontaneously takes fire and burns with the combination with oxygen of air. Here light is produced since the ignition point of P is reached during combination with oxygen of air. Now *slow combustion* is said to take place when slow oxidation occurs below the ignition point. Thus in the animal body, slow combustion of waste tissues takes place due to slow oxidation through the agency of oxygen of air inhaled and this slow combustion maintains the heat of the animal body. A similar operation takes place when iron rusts in air. Iron combines slowly with oxygen of the air, but during this slow oxidation neither any heat nor any light is visible. That actually iron, in case of rusting, combines with oxygen of air is proved by taking some moist iron nails in a small basin and floating it over water contained in a trough and then inverting a gas jar over the small basin in such a fashion that it covers the basin completely ; after the lapse of a few days, it is observed that water rises in the gas jar and fills about one-fifth of the total volume of air enclosed, when the rusting has taken place completely ; the residual gas can be proved to be nitrogen.

Thus, since rusting occurs due to slow combination with oxygen, it may be called slow combustion.

As it has been stated, rusting occurs through the production of hydrated ferric oxide of composition $2Fe_2O_3, 3H_2O$. After drying, it may be assumed that all the water is removed and Fe_2O_3 alone remains. The gain in weight indicates only the amount of oxygen added to iron from air. Hence 1·0714 gram was the weight of oxygen lost by air enclosed in the glass flask.

Now the glass flask contained 5 litres of air at N.T.P., of which 20% is oxygen and 80% is nitrogen. Therefore, the glass flask contained $\frac{5 \times 20}{100}$ or, 1 litre of oxygen at N.T.P. and (5 − 1) or 4 litres of nitrogen at N.T.P.

Now, since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P., therefore, 32 grams of oxygen will occupy 22·4 litres at N.T.P.

Hence, 1·0714 gram of oxygen will occupy $\frac{22{\cdot}4}{32} \times 1{\cdot}0714$ litre, *i.e.*, 0·74998 litre at N.T.P.

Therefore, 0·74998 litre of oxygen from 1 litre present in the glass flask was used up in forming the rust. Hence the flask contained, at the time when it was opened, 4 litres of nitrogen and 1—0·74998 litre or 0·25002 litre of oxygen, both measured at N.T.P.

Q. 5. *Describe the preparation of pure and dry sulphur dioxide. Give a neat sketch of the apparatus used. What reactions take place when the gas is led into :—*

(*a*) *Chlorine water,* (*b*) *Potassium hydroxide solution,* (*c*) *A mixture of nitrogen peroxide and water-vapour ?*

Ans. In the laboratory, sulphur dioxide is prepared in the following way :—Some copper turnings are taken in a flask fitted with a thistle funnel and a delivery tube. Concentrated H_2SO_4 is poured down the thistle funnel till the end of the funnel remains dipped under the surface of the acid. The flask is then placed on a piece of wire gauze and heated till the gas begins to be evolved. The source of heat is then removed and the gas is collected by the upward displacement of air. The gas is fairly dry and pure, but may be further dried by passing through a wash-bottle containing concentrated sulphuric acid and collected over mercury.

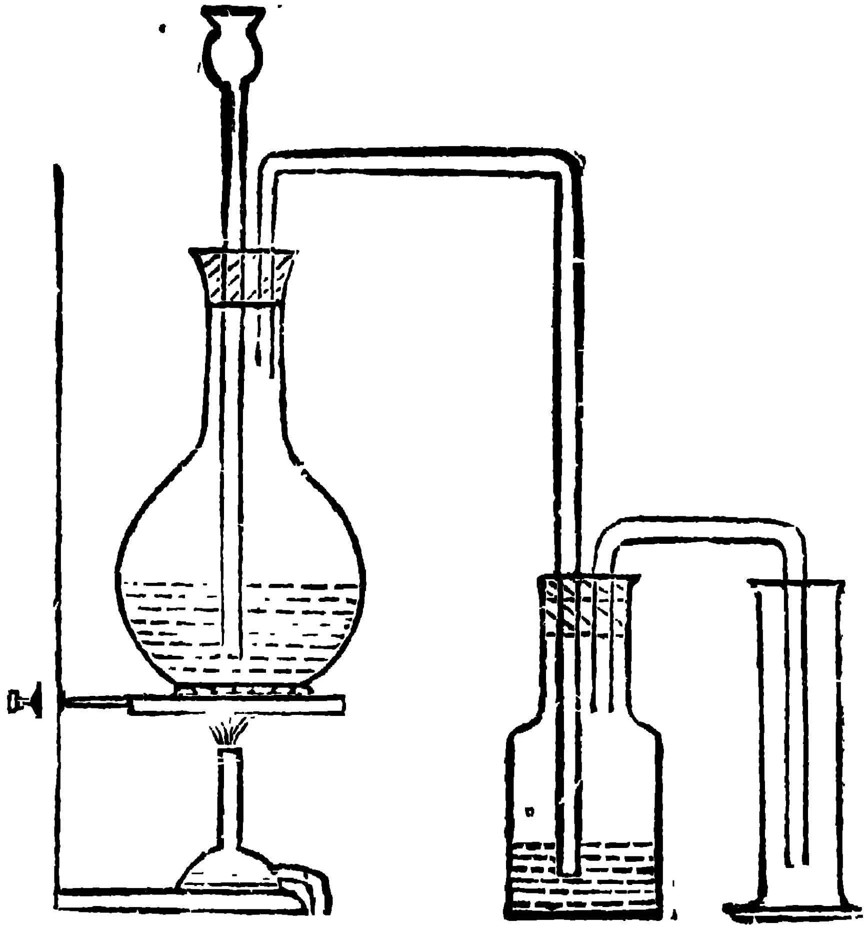


Fig. 18

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

(a) When sulphur dioxide is led into chlorine water, sulphuric acid is produced by oxidation of SO_2 to SO_3 which with water gives sulphuric acid, and reduction of chlorine takes place of hydrochloric acid.

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

(*b*) When sulphur dioxide is led into potassium hydroxide solution, at first potassium sulphite is formed, but on continued passage of SO_2, potassium bisulphite is produced in solution.

$$2KOH + SO_2 = K_2SO_3 + H_2O.$$
$$K_2SO_3 + SO_2 + H_2O = 2KHSO_3.$$

(c) When sulphur dioxide is led into a mixture of nitrogen peroxide and water-vapour, sulphuric acid is produced by oxidation of sulphur dioxide to sulphur trioxide by nitrogen peroxide, sulphur trioxide being converted into sulphuric acid by water-vapour present. Nitrogen peroxide, at the same time, is reduced to nitric oxide. This reaction occurs during the manufacture of sulphuric acid by the Chamber Process.

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

Q. 6. *How is sodium carbonate manufactured, by the "ammonia soda process" ?*

2 grams of a mixture of carbonate, bicarbonate and chloride of sodium gave, on gentle heating till no further evolution of gas occurred, 72 c.c. of carbon dioxide at 26°C. and 752 mm. pressure. 1·6 gm. of the same mixture required 26 c.c. of N HCl for complete neutralization. Calculate the percentage of carbonate, bicarbonate and chloride of sodium in the mixture (Na = 23·0, C = 12·0. O = 16·0, H = 1·0).

Ans. This process is based upon the reaction between hydrogen ammonium carbonate, NH_4HCO_3 and a strong solution of sodium chloride, according to the equation.

$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3.$$

The actual operation is carried out as follows : —

Carbon dioxide is passed into a solution of common salt (called brine) under moderate pressure after the brine is saturated with ammonia gas and cooled. Carbon dioxide first reacts with ammonia forming ammonium bicarbonate.

$$CO_2 + NH_3 + H_2O = NH_4HCO_3.$$

The bicarbonate of ammonium then reacts with sodium chloride forming sodium bicarbonate and ammonium chloride by double decomposition.

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

The above reaction is reversible and hence sodium chloride is partially converted into sodium bicarbonate. This sodium bicarbonate being sparingly soluble separates out, leaving the more soluble ammonium chloride in solution. The above reaction takes place most efficiently between 30° – 40°C. Sodium bicarbonate separating out is collected and converted into normal sodium carbonate by calcination.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The raw materials necessary are : (1) Brine, obtained directly from salt-beds, (2) Lime-stone for generating carbon dioxide, the lime left being used afterwards for recovering ammonia from residual ammonium chloride solution, (3) Ammonia.

The manufacturing process consists of *five* operations :—

(1) Saturation of brine with ammonia in ammonia-absorbers fitted with cooling arrangement.

(2) Carbon dioxide treatment of ammoniated brine in Solvay's carbonating towers under a pressure of 1—2 atmospheres.

(3) Filtration of the bicarbonate separating in Solvay's tower in vacuum filters.

(4) Calcination of the bicarbonate of sodium in order to get normal sodium carbonate and carbon dioxide which can be used over again.

(5) Recovery of ammonia from ammonium chloride solution by heating with lime, this ammonia being used over again. About 2% of ammonia is lost during working of the process and this is to be replaced. Hence it is found to be a self-contained operation and the working of the process is less costly in comparison to Leblanc process.

Sum. Of the three constituents Na_2CO_3, $NaHCO_3$ and $NaCl$ of the mixture, it is only $NaHCO_3$, which gives CO_2 on heating, according to the equation.

$$\begin{array}{lll} 2\ NaHCO_3 & = Na_2CO_3 + H_2O + CO_2 \\ 2\times(23+1+12+48) & \qquad\qquad 44 \\ \text{or,}\quad 168 & \end{array}$$

From the above equation, we know that

168 grams of sodium bicarbonate, on being decomposed by heating, give 44 grams of carbon dioxide, *i.e.*, 22·4 litres of CO_2 at N.T.P., since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P. Now CO_2 evolved from the sodium bicarbonate present in 2 grams of the mixture is 62 c.c. at

26°C. and 752 m.m. pressure. Let V be the volume of this CO_2 at N.T.P. Then by Boyle's and Charles' laws, we have

$$\frac{62 \times 752}{273+26} = \frac{V \times 760}{273}.$$

$$\text{when} \quad V = \frac{62 \times 752 \times 273}{299 \times 760} \text{ c.c,}$$

$$= 56{\cdot}02 \text{ c.c.}$$

Now 22400 c.c. of CO_2 at N.T.P. is evolved from 168 grams of $NaHCO_3$.

∴ 56·02 c.c. of CO_2 at N.T.P. is given by $\frac{168}{22400} \times 56{\cdot}02$ gram or 0·4202 gram of $NaHCO_3$. Hence, 2 grams of the mixture contained 0·4202 gram of $NaHCO_3$.

Therefore, 1·6 grams of the mixture contained $\frac{0{\cdot}4202}{2} \times 1{\cdot}6$ gram or 0·33616 gram of $NaHCO_3$.

Now, from the equation,

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

We know that,

84 grams of sodium bicarbonate require 36·5 grams of HCl for neutralisation. But 36·5 grams of HCl are contained in 1000 c.c. of N HCl solution. Therefore, to neutralise 84 grams of sodium bicarbonate, 1000 c.c. of N HCl are required. Hence to neutralise 0·33616 gram of $NaHCO_3$, the amount of N HCl required $\frac{1000}{84} \times 0{\cdot}33616$ c.c. $= 4{\cdot}00$ c.c.

Hence of the 26 c.c. of N HCl used for complete neutralisation of the mixture, 4 c.c. of N HCl were required for the bicarbonate of sodium present in it. Therefore, $26 - 4$ or 22 c.c. of N HCl were required for netralisation of Na_2CO_3 present in the mixture.

Now, 22 c.c. of N HCl ≡ 22 c.c. of N Na_2CO_3. Therefore, Na_2CO_3 present in the mixture $= \frac{22 \times 53}{1000}$ grams $= 1{\cdot}166$ grams since 1000 c.c. of N Na_2CO_3 contain 53 grams of Na_2CO_3.

Hence, 1·6 grams of the mixture supplied contained 1·166 grams of Na_2CO_3, 0·33616 gram of $NaHCO_3$ and $1·6-(1·166+0·33616)$ or 0·09784 gram of NaCl.

Therefore, the percentage of $NaHCO_3 = \frac{0·33616}{1·6} \times 100$

$= 21·01$

„ „ „ $Na_2CO_3 = \frac{1·166}{1·6} \times 100$

$= 72·875$

„ „ „ $NaCl = \frac{0·09784}{1·6} \times 100$

$= 6·115.$

Q. 7. *Name the principal ores of zinc with their formulæ. How is the metal extracted from them? State the uses of the metal and its important alloys.*

Describe the action of nitric acid upon the metal.

Ans. The important ores of zinc are

(1) Calamine or zinc spar—$ZnCO_3$

(2) Zinc blende or black-jack—ZnS.

Other ores are (3) Red zinc ore—ZnO

(4) Franklinite—$(Zn.\ Fe)\ O,\ Fe_2O_3$.

The most important ore, zinc blende, ZnS, is found to be associated with galena (PbS), quartz, sand, etc. To remove these the crushed ore is mixed with a little oil and stirred up with water when zinc blende rises to the surface and is thus separated from galena, sand, etc. which remain at the bottom. The carbonate ore, zinc spar, is also used for this purpose.

The process of extraction consists of two operations, namely: first, the conversion of the ore into oxide of zinc, by roasting; and secondly, the reduction of the oxide by means of coal at a high temperature.

Purified ZnS is roasted in a multiple hearth furnace and is oxidised to ZnO. Care is taken to see that it is transformed as completely as possible into ZnO and not into $ZnSO_4$.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The roasting of natural carbonate is readily accomplished, this compound merely giving off its CO_2 at a high temperature—

$$ZnCO_3 = ZnO + CO_2.$$

The operation here is known as *calcination.*

The roasted ore is then mixed with powdered coke and introduced in fire-clay retorts, which are strongly heated ; ZnO is reduced at 1000°C. to zinc, which distils off being volatile : $ZnO + C = Zn + CO$. *The Belgian retorts* are fire-clay tubes closed at one end, with iron tubes as receivers in which zinc condenses and solidifies. *Silesian retorts* are muffle furnaces with receivers of iron luted with fire-clay. About 10—25% of Zn is lost due to oxidation of zinc and formation of zinc-dust, etc. Excess of carbon is used in the operation so that formation of CO_2 is prevented as CO_2 oxidises zinc.

Uses of zinc.—Zinc is used for galvanizing iron sheets, for the manufacture of vats, tanks and pipes, for the electrodes of electric cells, in the extraction of gold and silver, for the production of hydrogen and as a reducing agent in the laboratory, specially in the form of zinc-dust.

Important alloys of zinc are ordinary brass, Dutch metal, German silver and bronze. Brass is used for manufacture of utensils, German silver is used for preparation of artistic vessels as also for ordinary utensils, bronze is used in coinage and for preparation of statues.

With nitric acid zinc gives zinc nitrate. If the acid is concentrated, nitrogen peroxide is mainly produced ; if weaker acid is used, nitric oxide is the chief product. Dilute nitric acid gives no gaseous product, but gives ammonium nitrate.

$$Zn + 4HNO_3 = Zn\,(NO_3)_2 + 2H_2O + 2NO_2$$
$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO$$
$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

Q. 8. *Describe an experiment in illustration of each of the following :—*

(*a*) *Formation of a solid by the mixing of two gases.*

(*b*) *Promotion of chemical change by light.*

(*c*) *Burning in an atmosphere of carbon dioxide.*

(*d*) *Chemical reaction by means of electric arc.*

(*e*) *Generation of heat when two liquids in the cold are mixed together.*

Ans. (*a*) Two gas jars are taken. One of them is filled up with partially dried ammonia gas and the other one with nearly dry hydrogen chloride. The two jars are then placed mouth to mouth. Dense white fumes of ammonium chloride are produced and these gradually settle as a solid powder at the bottom.

$$NH_3 + HCl = NH_4Cl.$$

(*b*) A gas jar is filled up with carbon monoxide and another jar is filled up with chlorine, the two jars are then placed mouth to mouth and the gases are thoroughly mixed inside a room. The mixture is then exposed to direct sunlight. CO and Cl_2 combine giving carbonyl chloride or *phosgene gas.*

$$CO + Cl_2 = COCl_2.$$

(*c*) A gas-jar is filled with carbon dioxide gas and then burning magnesium ribbon is introduced into it. The magnesium ribbon continues to burn with separation of soot.

$$2Mg + CO_2 = 2MgO + C.$$

(*d*) Two carbon electrodes are fitted to a glass globe provided with an inlet and an outlet tube. A current of hydrogen is introduced through the inlet tube and air is completely displaced from the glass globe. An arc is then struck between the two carbon pencils. Carbon and hydrogen combine under the influence of electric arc, giving acetylene which escapes by the outlet tube.

$$2C + H_2 = C_2H_2.$$

(*e*) Cold water is taken in a beaker. Conc. H_2SO_4 from a bottle is then poured in a thin stream into the cold water with constant stirring. The mixing of the two liquids generates so much heat that water is converted into steam which escapes from the mixture.

1943

SECOND PAPER

Q. 1. *A specimen of chalk contained calcium sulphate as impurity. One gram of the solid was allowed to be in contact with 230 c.c. of N/10 hydrochloric acid solution. The excess of acid in the mixture was completely neutralised by 80 c.c. of ·45N caustic soda solution. Calculate the percentage of chalk in the specimen.*

How much carbon dioxide measured at 25°C. and 756 mm. will be obtained by the complete decomposition of 40 grams of this chalk?

(At. wt. of $Ca = 40$, $Na = 23$, $O = 16$, $H = 1$ and $Cl = 35·5$)

Ans. 80 c.c. of 0·45 N caustic soda $\equiv 80 \times 0·45$ c.c. of N caustic soda $\equiv 36·00$ c.c. of N caustic soda $\equiv 36$ c.c. of N HCl.

But HCl sol. allowed to react with the specimen of chalk $=$ 230 c.c. of $\frac{N}{10}$ HCl $= 23$ c.c. of N HCl.

So, from the given data, we find that caustic soda solution used to neutralise the excess of acid is far greater than the acid actually used. So the given data are absurd and so the sum cannot be worked out.

Second part of the sum cannot be worked out unless the percentage of calcium carbonate can be found out.

Q. 2. *What are the present-day ideas about an atom?*

What do you mean by the term 'atomic weight'? How have the atomic weights of elements been determined?

Ans. Structure of an atom.—Dalton's Atomic theory postulates atom as an indivisible unit in the structure of matter, and it was supposed that atom could not be further broken up into simpler constituents. But this conception about atom underwent a radical change through the researches of several scientists like Sir J. J. Thomson, Sir E. Rutherford and others. These scientists have shown that an atom can be broken up into simpler constituents, *viz.*, electrons, protons and neutrons, to which a fourth one has very recently been added, *viz.*, positron.

Electrons are negatively charged particles, each carrying a unit negative charge. The mass of each electron is found to be about 1/1850 of the mass of a hydrogen atom.

Protons are positively charged particles each, carrying a unit positive charge. The mass of each proton is nearly the same as that of a hydrogen atom.

Neutrons are particles each of which is of nearly the same mass as that of hydrogen atom but are electrically neutral. The true nature of these particles has not yet been determined. Each one of these particles is considered by some scientists as being produced by close union of electron and proton : others are of opinion that each neutron is a fundamental particle and each proton is produced by close union of 1 neutron and 1 positron.

Positrons are said to be the exact counterparts of the electrons. Each positron has the mass of nearly $\frac{1}{1850}$th of that of the hydrogen atom, but unlike the electron, it carries unit positive charge of electricity.

The structure of the atom, as suggested in Rutherford-Bohr model, is known as the nuclear structure of the atom. The atom is regarded at present as a system consisting of a core or nucleus, carrying positive charge and surrounded by a number of electrons. Since the atom is electrically neutral, the number of electrons surrounding the nucleus of an atom is the same as the net positive charge carried by the nucleus. The nucleus is made up of protons, electrons, neutrons and probably positrons. There are also electrons outside the nucleus, known as extra-nuclear electrons, arranged in different layers known as orbits of electrons. The positive charge of the nucleus is equal to the sum-total of the negative charges carried by extra-nuclear electrons. The net positive charge on the nucleus of the atom is known as atomic number. Since the mass of the electron is negligible in comparison to the mass of the proton and neutron, the whole mass of the atom must be located in the nucleus and this must be equal to the sum-total of the number of neutrons and protons present in the nucleus. Protons are probably identical with the positively charged nuclei of hydrogen atoms, *i.e.*, hydrogen atoms each of which has been shorn of one electron.

On this view, the helium nucleus is to be regarded as composed of four hydrogen nuclei with two cementing electrons, leaving it with a net positive charge of two units. So there are two extra nuclear electrons in an orbit surrounding the nucleus so that the helium atom as a whole is electrically neutral.

Atoms of the same element have all the same net positive charges in their nuclei, but atoms of different elements carry different amounts of net positive charges in their nuclei. Atoms of the same element will always carry the same net positive charge in their nuclei, but may not possess the same atomic masses, due to different number of protons, neutrons and electrons being present in their core. In that case these are called *isotopes*. The isotopes have the same atomic number and hence identical chemical properties, but different atomic masses.

Though an atom is regarded at present to be divisible into simpler constituents, yet chemically it is regarded as a separate entity taking part in all chemical changes as a separate unit.

The *atomic weight* of an element is the ratio of the weight of one atom of the element to the weight of one atom of hydrogen. Thus, the atomic weight of an element is not actually the weight of an atom of that element but it is simply a number. Also the atomic weight of an element is the smallest weight of it present in the molecular weight of any of its compounds.

When we say, that the atomic weight of oxygen is 16, we mean that one atom of oxygen is 16 times as heavy as an atom of hydrogen. It also means that the smallest weight of oxygen present in the molecular weight of any of its compounds is 16.

Various methods available for the determination of atomic weight of an element are—

(1) By application of Dulong and Petit's Law for atomic heat and subsequently using the relation Atomic weight = Equivalent weight × Valency.

(2) By application of Mistcherlich's Law of isomorphism.

(3) From determination of vapour density of volatile compounds of the element, and quantitative chemical analysis of the compounds.

(4) From the position of the element in the Periodic Table of elements.

(1) For solid elements, save and except a few, *viz.*, C, B, Si, Dulong and Petit found that *the product of atomic weights and the respective specific heats came out in most cases to be approximately 6·4.*

Thus At. wt. × Sp. heat = 6·4 (app.)

This is an approximate law, for the value 6·4, for the product which is called atomic heat, is not a constant but varies within narrow limits.

For determination of the atomic weight, first the sp. heat of the element is determined and then by dividing 6·4 by the sp. heat so determined, we can get an approximate At. weight of the element.

Thus, *Atomic weight* $= \frac{6 \cdot 4}{\text{Specific heat}}$ (approx.)

Then the equivalent weight of the element is determined very carefully and accurately. Next the approximate atomic weight is divided by the equivalent weight in order to find the valency. It may come out to be a fraction, but valency cannot be fractional, so the nearest whole number is taken as the valency of the element. Then, by using the relation, Atomic weight = Equivalent weight × valency, the exact atomic weight of the element is determined.

Illustration.—The Sp. heat of a metal is found by experiment to be 0·25. Its equivalent weight is found by experiment to be 12. Then

Approximate At. wt. $= \frac{6 \cdot 4}{0 \cdot 25} = 25 \cdot 6$

Hence, valency of the element $= \frac{25 \cdot 6}{12} = 2 \cdot 13$.

Thus the valency = 2, taking the nearest whole number,

Therefore, the true At. wt. of the element = 12 × 2 = 24.

(2) Mitscherlich, in 1819, put forth the law that :—

When two compounds are isomorphous with each other, they are usually composed of the same number of similar atoms combined in a similar manner. In a pair of isomorphous compounds, therefore, at least one element appears to have been replaced, atom for atom, by another element and the weights of the elements thus replaced mutually are proportional to their atomic weights. If the atomic weight of one of the elements is known, that for the other can be calculated.

Example. Potassium chromate is found to be isomorphous with potassium sulphate and is found to contain 26·78 per cent. of Cr. From this the at. wt. of Cr can be calculated thus :—

Potassium sulphate has the formula K_2SO_4 and since potassium chromate is isomorphous with it, its formula is K_2CrO_4. Let x be the at. wt. of Cr. Then the molecular weight of K_2CrO_4 is $39{\cdot}1 \times 2 + x + 16 \times 4 = 78{\cdot}2 + 64 + x = 142{\cdot}2 + x$. Therefore the percentage of Cr in it $= \dfrac{100 \times x}{142{\cdot}2 + x} = 26{\cdot}78$, (given) whence $x = 52$.

(3) In order to find out the atomic weight of an element, the molecular weights of a number of its volatile compounds are first of all calculated from their experimentally determined vapour densities. Next the weight of the element in the molecular weights of each of these compounds is determined by quantitative chemical analysis. The smallest of these different weights of the element found in the molecular proportions of its compounds is the atomic weight, since no molecule can contain less than one atom of the element under consideration.

Example. In order to determine the atomic weight of oxygen, several volatile compounds containing oxygen are taken and their vapour densities determined by the usual methods. Next by analysis the proportion of oxygen in molecular proportion of each of the compounds found out, and the lowest of these weights *viz.*, 16, is accepted as its atomic weight.

Compound	Vapour density	Molecular weight	Percentage of oxygen as found by analysis indirectly	Actual weight of O, in molecular weight of the compound
Carbon dioxide	22	44	72·72	32
Carbon monoxide	14	28	57·14	16
Sulphur dioxide	32	64	50·00	32
Nitrous oxide	22	44	36·36	16
Nitric oxide	15	30	53·33	16
Sulphur trioxide	40	80	60·00	48

If at any time any compound of oxygen be discovered in which the amount of oxygen found in the molecular weight of that compound be less than 16, then this value 16 would be rejected and the lowest value found would be accepted as its at. wt. But so long as no such compound is found out, 16 is accepted as the atomic weight of oxygen.

(4) From the position of an element in the Periodic Table, atomic weight of the element can be found out approximately.

Example. Thus, for determining the at. wt. of Bromine, we note the atomic weight of four elements on four sides of it, *viz.* Chlorine 35·46, Iron 55·84, Iodine 126·92 and Tc 99·00.

The mean of these is the atomic weight of Bromine, thus, $\frac{35{\cdot}46+55{\cdot}84+126{\cdot}92+99{\cdot}00}{4}=\frac{317{\cdot}22}{4}=79{\cdot}3$, the exact value being 79·92.

Q. 3. *Describe an experiment to determine the equivalent weight of potassium.*

1·49 grams of potassium chloride gave 2·87 grams of silver chloride. Calculate the equivalent weight of potassium.

Ans. Equivalent weight of Potassium :—

A weighed quantity of pure re-crystallised potassium chloride is taken in a beaker and is then dissolved completely in distilled water. The solution is next made *slightly acidic* with dilute nitric acid. Then silver nitrate solution is slowly added with constant stirring until the precipitated silver chloride coagulates and settles at the bottom. A few drops more of silver nitrate solution is then added to see that the precipitation is complete and no more turbidity appears where the two solutions meet,

$$KCl+AgNO_3=AgCl+KNO_3.$$

The liquid is then heated and filtered through a Gooch crucible, previously prepared and weighed to a constant weight. The precipitate is thoroughly washed with distilled water to free it from adhering silver nitrate and potassium nitrate. Then the Gooch crucible is dried in an air-oven, cooled in a desiccator and weighed. Heating in an air-oven, cooling in a desiccator and weighing is continued till the final weight is constant. The difference between the two weighings of the Gooch crucible will give the weight of AgCl produced from a known weight of KCl.

Calculation :

Let the weight of KCl taken $= w_1$ gms.
and the weight of AgCl formed $= w_2$ gms.

Now, in $(108 + 35\cdot5)$ or $143\cdot5$ parts by weight of AgCl, there are 35·5 parts by weight of chlorine.

$\therefore$ in w_2 gms of AgCl, we have $\dfrac{w_2 \times 35\cdot5}{143\cdot5}$ gms. of chlorine.

And this amount of chlorine has come from w_1 gms. of KCl. Hence the weight of K present in w_1 gms. of $\text{KCl} = w_1 - \dfrac{w_2 \times 35\cdot5}{143\cdot5} = w_3$ gms., say.

Then, $\dfrac{w_1 \times 35\cdot5}{143\cdot5}$ gms. of chlorine has combined with w_3 gms. of K.

$\therefore$ 35·5 gms. of chlorine can combine with

$$\frac{w_3}{\dfrac{w_2 \times 35\cdot5}{143\cdot5}} \times 35\cdot5 \text{ gms.} = \frac{w_3 \times 143\cdot5}{w_2} \text{ gms. of K.}$$

Hence, by definition, the equivalent weight of potassium

$$= \frac{w_3 \times 143\cdot5}{w_2}.$$

Since 143·5 grams of silver chloride contain 35·5 grams of chlorine,

therefore, 2·87 grams of silver chloride will contain $\dfrac{35\cdot5 \times 2\cdot87}{143\cdot5} =$ or, $35\cdot5 \times 0\cdot02$ grams of chlorine, or, 0·71 grams of chlorine.

This amount of chlorine has come from 1·49 grams of potassium chloride.

Hence 0·71 grams of chlorine has combined with $(1\cdot49 - 0\cdot71)$ or 0·78 grams of potassium.

Therefore, by definition, the equivalent weight of potassium is that weight of it which will combine with 35·5 grams of chlorine, and hence the equivalent weight of potassium $= \frac{0{\cdot}78}{0{\cdot}71} \times 35{\cdot}5 = 39$.

Q. 4. *How is phosphorus prepared?*

How is white phosphorus converted into the red variety and **vice versa?**

Ans. Naturally occurring calcium phosphate is now-a-days utilised for getting phosphorus on a large scale. A mixture of phosphate, sand and coke is fed through a feed-hopper into a closed electric furnace made of brick-work provided with an outlet above for the gases and phosphorus vapour, a slag hole at the bottom and carbon electrodes, set nearly at the bottom, between which an electric arc is struck, producing a very high temperature.

The silica of the sand reacts at the high temperature of the furnace with calcium phosphate producing calcium silicate and phosphorus pentoxide, P_2O_5.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

The vapour of P_2O_5 is then reduced by carbon and carbon monoxide is formed and phosphorus is set free.

$$P_2O_5 + 5C = 2P + 5CO.$$

Calcium silicate melts and sinks to the bottom from where it is run off as a slag through the slag hole. Phosphorus vapour

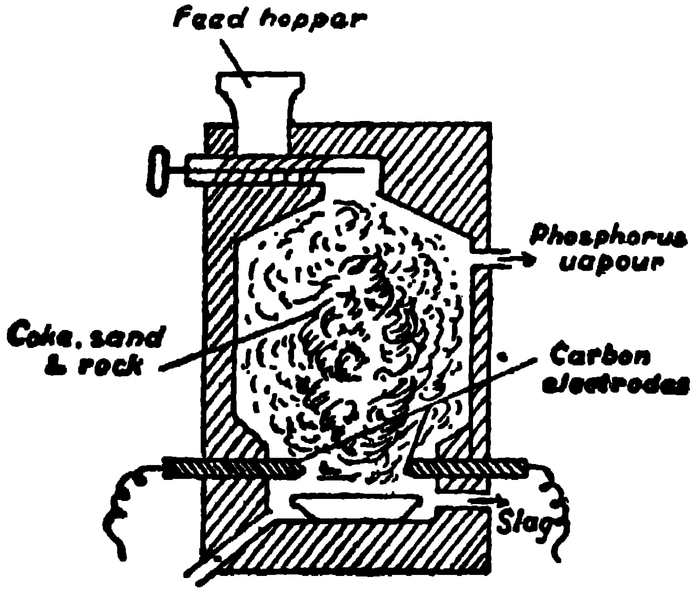


Fig. 19

and carbon monoxide escape through the outlet near the top and are passed into water where P_4 vapour condenses. Fresh mixture is introduced through the feed-hopper and the process is continuous.

White phosphorus is converted into red phosphorus when it is heated to 250°C. in an inert atmosphere in presence of a trace of iodine.

Red phosphorus, on the other hand, is converted into white phosphorus by heating it in an inert atmosphere to above 550°C. until vapours are produced. By rapidly cooling the vapours white phosphorus is obtained.

Q. 5. *In an alkali factory chlorine is a by-product. How can this be best utilised ?*

How does the action of chlorine on milk of lime vary according to the conditions of temperature ? Represent the reaction by equations.

Ans. Chlorine is obtained as a by-product in an alkali factory, either during the manufacture of caustic soda by the electrolysis of brine by Castner-Kellner process or during the manufacture of sodium carbonate by the electrolysis of brine by Hargreaves-Bird process. The chlorine is evolved at the anode during electrolysis. This chlorine can be best utilised for the manufacture of bleaching powder. The chlorine is led away by means of exit pipes into an air-tight chamber lined with lead on the floor of which slaked lime is spread to the depth of a few inches. The temperature is not allowed to rise above 35°C.—40°C. The lime is raked on from time to time so as to expose fresh portions of it to the action of chlorine. The reaction takes about 24 hours for completion. A little quantity of lime is dusted at the end into the chamber by special fan arrangements to effect complete absorption of chlorine. Bleaching powder is then taken out by removing the false bottom of the floor and put into air-tight barrels.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

When chlorine is passed into cold milk of lime containing excess of water in such a fashion that excess of the alkali remains, calcium chloride and calcium hypochlorite are produced.

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

When chlorine is passed into hot milk of lime containing less quantity of water in such a fashion that excess of chlorine is passed in, calcium chlorate and calcium chloride are obtained.

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

Q. 6. *Discuss the changes that take place when :—*

(*a*) *a solution of caustic soda is added to a solution of zinc sulphate ;*

(*b*) *stannous chloride is added to a solution of mercuric chloride ;*

(*c*) *ammonia is added to a solution of copper sulphate ;* and

(*d*) *magnesium chloride hexahydrate is heated alone.*

Ans. (*a*) When a solution of caustic soda is added drop by drop to a solution of zinc sulphate, at first a white precipitate of zinc hydroxide is formed, but on addition of excess of caustic soda solution, the precipitate of zinc hydroxide dissolves forming sodium zincate and water.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

(*b*) When stannous chloride solution is added drop by drop to mercuric chloride solution, at first a white precipitate of mercurous chloride is formed, but on addition of excess of stannous chloride solution grey metallic mercury is deposited. Mercuric chloride is here reduced first to mercurous chloride and then to grey metallic mercury, stannous chloride being oxidised in each case to stannic chloride.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 - SnCl_2 = 2Hg + SnCl_4.$$

(*c*) When a solution of ammonia is added slowly to a solution of copper sulphate, at first a bluish-white precipitate of basic copper sulphate, $Cu_2(OH)_2SO_4$, which gradually changes to cupric hydroxide, $Cu(OH)_2$, is obtained. On adding further quantity of ammonia solution, the precipitate dissolves producing a deep blue solution of cuprammonium sulphate, $Cu(NH_3)_4SO_4$. [The solution deposits blue rhombic crystals, which when dried over lime, have the composition $Cu(NH_3)_4SO_4,H_2O$.]

$$NH_3 + H_2O = NH_4OH$$
$$2CuSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Cu_2(OH)_2SO_4$$
$$Cu_2(OH)_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2Cu(OH)_2$$
$$Cu(OH)_2 + 4NH_4OH = Cu(NH_3)_4(OH)_2 + 4H_2O$$
$$Cu(NH_3)_4(OH)_2 + (NH_4)_2SO_4 = Cu(NH_3)_4SO_4 + 2NH_4OH.$$

or final reaction is represented by the equation

$$CuSO_4 + 4NH_4OH = Cu(NH_3)_4SO_4 + 4H_2O.$$

(*d*) When magnesium chloride hexahydrate is heated alone, it first melts and is then partially dehydrated and five molecules of water are driven off.

$$MgCl_2, 6H_2O = MgCl_2, H_2O + 5H_2O.$$

On further heating magnesium chloride monohydrate decomposes giving magnesium oxide and hydrochloric acid.

$$MgCl_2, H_2O = MgO + 2HCl.$$

According to some chemists, above 180°C., Magnesium chloride hexahydrate undergoes hydrolytic decomposition with evolution of hydrogen chloride and formation of magnesium oxychloride.

$$2(MgCl_2, 6H_2O) = 11H_2O + Mg_2OCl_2 + 2HCl.$$

On further heating in air, magnesium oxychloride decomposes giving magnesium oxide and chlorine.

$$2Mg_2OCl_2 + O_2 = 4MgO + 2Cl_2.$$

Q. 7. *Describe the method for the preparation of metallic sodium. Give a neat diagram of the apparatus employed for the purpose ? What precautions are necessary ? Mention the uses of the metal.*

Ans. Now-a-days sodium is almost exclusively prepared by electrolytic methods, by electrolysis of either fused caustic soda (Castner's Process) or of fused sodium chloride (Down's Process).

Castner's Process.—Caustic soda is contained in an iron pot *P*, set in a suitable brick work, and is kept in a melted condition by gas flames below.

Through the bottom of this vessel passes an iron rod kept in the vertical position by the caustic soda in the lower and narrow parts of the vessel, being in the solidified state. The anode is a cylinder of nickel suspended from above surrounding the cathode, and is prevented from touching it by means of a nickel wire-gauze cylinder which hangs from a cylindrical iron vessel which is open at the bottom and provided with a lid at the top and is hanging from the top of the iron vessel just above the iron cathode. Electric current is passed by connecting the electrodes to the poles of a battery. The fused caustic soda is decomposed. Sodium is liberated at the cathode, and being lighter than fused NaOH, rises up to the surface and collects inside the iron vessel hanging over the cathode, in which hydrogen also collects. This hydrogen protects sodium from oxidation. The excess of hydrogen escapes through the lid. Oxygen escapes after being liberated at the anode through an outlet at the top. Sodium is removed by means of perforated ladles from time to time and kept under Kerosine-oil.

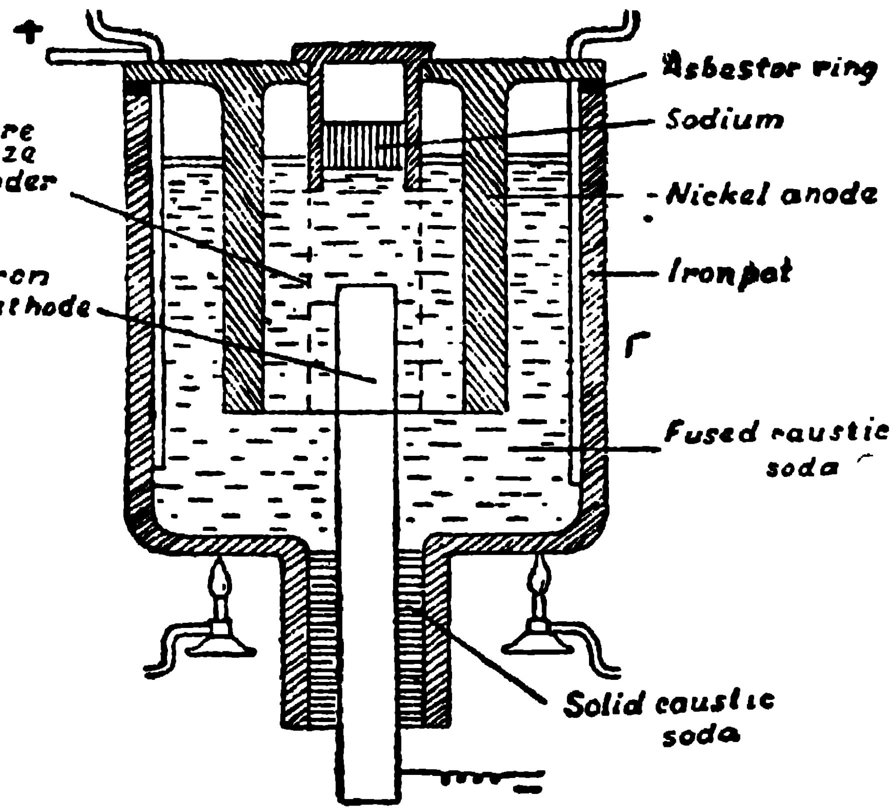


Fig. 20

$$2NaOH = \underbrace{2Na + H_2}_{\text{Cathode}} + \underset{\text{anode.}}{O_2.}$$

Sodium is also obtained from common salt by the electrolytic process as applied to fused common salt.

In the **Down's cell**, the operation is carried out by introducing sodium chloride or common salt, mixed with sodium fluoride or $CaCl_2$ to lower its melting point, through an opening *b* at the top and fused by heating. The carbon anode *a* is introduced through the base and is surrounded by a cylindrical iron cathode *C*. At the top of the anode there is a dome-shapped hood *A* for leading away the chlorine. The cathode is surrounded by an iron wire-gauze mantle, at the top of which is a vertical pipe *P*, communicating with a closed vessel *R*. Current is now passed through the molten electrolyte, when NaCl alone is decomposed but not NaF or $CaCl_2$. Chlorine evolved at the anode escapes through *A*, whereas sodium liberated at the cathode collects inside the mantle inverted over *C*. Gradually the level of sodium rises in the pipe *P* and sodium ultimately flows into the reservoir *R*.

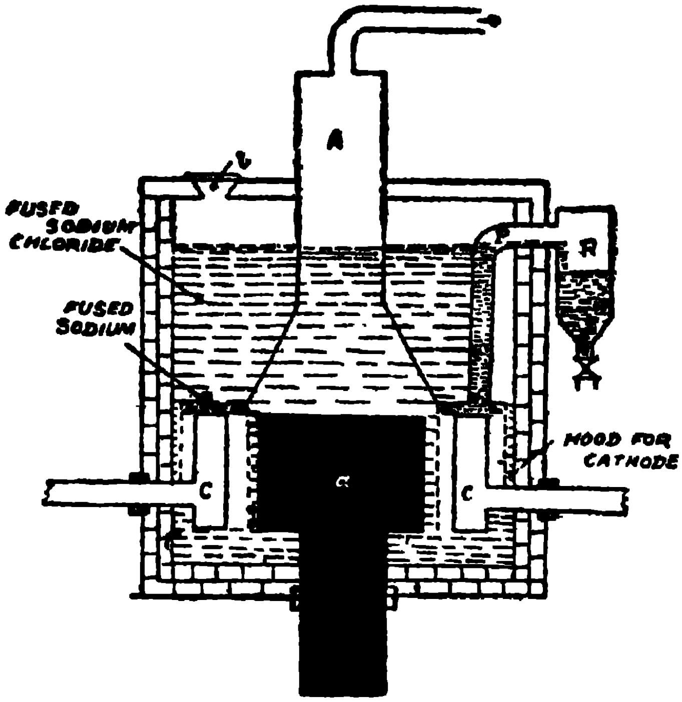


Fig. 21

Precautions necessary in operating Castner's process are :—

(*a*) The nickel anode is to be electrically insulated from the iron cathode.

(*b*) The temperature of the fused caustic soda is to be kept at 330°C., as otherwise the molten sodium will remain dissolved in fused caustic soda.

(*c*) Hydrogen in the iron vessel should be allowed to escape at a slow rate, so that Na liberated and collected therein may remain entirely in the atmosphere of hydrogen.

Uses of sodium.—Sodium is used for the manufacture of sodium peroxide, sodium cyanide ; for the extraction of metallic magnesium, aluminium, elementary boron and silicon. Sodium amalgam is used as a reducing agent. An alloy of sodium and potassium is used in high temperature thermometry.

Q. 8. *The gaseous product obtained by burning pyrites is led into a large vat containing an aqueous solution of soda ash. The process is continued until the solution becomes saturated. From this solution now a crystalline solid separates out. What is this compound ? Support your statement by equations.*

The final product of the above reactions was treated with (*a*) *nitric acid,* (*b*) *sulphuric acid and* (*c*) *bromine water separately. Explain the changes that occur.*

Ans. The gaseous product obtained by burning pyrites is sulphur dioxide.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

Soda-ash is sodium carbonate, Na_2CO_3.

When SO_2, the gaseous product obtained by burning pyrites, is led into an aqueous solution of soda-ash, at first sodium sulphite is produced in solution.

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2.$$

The passage of SO_2 being continued until the solution becomes saturated, Na_2SO_3 is converted into sodium bisulphite, $NaHSO_3$, which remains in solution.

$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3.$$

From this solution of sodium bisulphite, on crystallisation, *sodium metabisulphite,* $Na_2S_2O_5$, crystallises out in the solid state.

$$2NaHSO_3 = Na_2S_2O_5 + H_2O.$$

Sodium bisulphite does not crystallise (Partington).

(*a*) When sodium metabisulphite is treated with nitric acid, it is oxidised to sodium bisulphate and nitric acid is reduced to oxides of nitrogen.

$$Na_2S_2O_5 + 2HNO_3 = 2NaHSO_4 + NO + NO_2.$$

(b) When sulphuric acid is added to sodium metabisulphite, sulphur dioxide is evolved and sodium bisulphate is formed.

$$Na_2S_2O_5 + 2H_2SO_4 = 2NaHSO_4 + H_2O + 2SO_2.$$

(c) Bromine water oxidises sodium metabisulphite to sodium bisulphate and is itself reduced to hydrobromic acid.

$$Na_2S_2O_5 + 3H_2O + 2Br_2 = 2NaHSO_4 + 4HBr.$$

1944

FIRST PAPER

Q. 1. *Explain and illustrate Gay Lussac's Law of Gaseous Volumes and show how it has led to the distinction between atoms and molecules.*

How would you prove that the density of a gas with respect to hydrogen is equal to half its own molecular weight?

Ans. Gay Lussac's Law of Gaseous Volumes :—

When chemical action takes place between gases, either elementary or compound, they react in volumes which bear a simple ratio to one another and also to the volume of the product, if gaseous (all volumes being measured under the same conditions of temperature and pressure).

The law rests upon experimentally established facts Thus from experiments, we know that

1 vol. of hydrogen reacts with 1 vol. of chlorine producing 2 vols. of hydrochloric acid gas (volume ratio is 1 : 1 : 2)

2 vols. of hydrogen combine with 1 vol. of oxygen giving rise to 2 vols. of steam (volume ratio is 2 : 1 : 2)

1 vol. of nitrogen reacts with 3 vols. of hydrogen forming 2 vols. of ammonia (volume ratio is 1 : 3 : 2).

This law of gaseous volumes thus states that simple relationship exists between volume of gases when they react chemically. A few years before the statement of Gay Lussac's law, it was established by Boyle and Charles that all gases behave similarly with change of pressure and temperature. Now Dalton postulated the 'atomic constitution of matter and explained all the laws of chemical combination by weight with the help of his Atomic Theory.

It was suggested that Dalton's Atomic theory would also provide a ready explanation of Gay Lussac's law of Gaseous volumes, based on experimental facts. Dalton's Atomic theory postulates that chemical action always takes place between a simple number of atoms of different elements and Gay Lussac's law establishes that chemical action takes place in case of gases by simple volume relations. Led by these considerations Berzelius suggested that *equal volumes of all gases under the corresponding conditions of temperature and pressure contain the same number of atoms.* At the time when this statement was made, no distinction was drawn between the ultimate particles of elements and the ultimate particles of compounds. Dalton named the ultimate particles of compounds as compound atoms, but his ideas were not clear in this respect.

Now this hypothesis of Berzelius could not explain the actual experimental facts. For example, we know from actual experiment

2 vols. of hydrogen combining with 1 vol. of oxygen give rise to 2 vols. of steam.

Let n be the number of 'atoms' present in 1 vol. of hydrogen. Then from the statement of Berzelius, $2n$ atoms of hydrogen combining with n atoms of oxygen produce $2n$ atoms of steam.

Or, 2 atoms of hydrogen combining with 1 atom of oxygen produce 2 atoms of steam.

Hence, 1 atom of steam contains $\frac{1}{2}$ atom of oxygen. Thus, every atom of oxygen must be broken up into half an atom to produce two atoms of steam. This is directly against Dalton's Atomic theory, which postulates that atoms are indivisible. Thus the hypothesis of Berzelius fails.

To get over this difficulty Avogadro, an Italian physicist, in 1811, drew up a distinction between the ultimate particles of elements which are indivisible and which can take part in chemical reactions, and the ultimate particles of elements and compounds which can exist in the free state retaining all the properties of the particular element or compound. He called the former particles *atoms* and the latter particles *molecules*. When chemical reaction takes place, molecules first break up into atoms and atoms then take part in chemical action as suggested in Dalton's Atomic theory. The molecule of a compound differs from that of an element in the sense that whereas the molecule of a compound is composed of different kinds of atoms, the molecules of elements are made up of the same kind of atoms. An atom is the smallest particle of an element that is found to be present in a molecule of any of its compounds.

Avogadro then modified the hypothesis of Berzelius and stated that *equal volumes of all gases, elementary or compound, under the same conditions of temperature and pressure, contain the same number of molecules.*

By applying this hypothesis to the case cited above, if n be the no. of molecules present in each volume of the gas, we shall have $2n$ molecules of hydrogen combining with n molecules of oxygen produce $2n$ molecules of steam or, 2 molecules of hydrogen combining with 1 molecule of oxygen produce 2 molecules of steam. Now each molecule of steam will contain at least 1 atom of oxygen and 2 molecules of steam will contain at least 2 atoms of oxygen. These 2 atoms of oxygen, therefore, must have come from 1 molecule of oxygen, or oxygen molecule contains at least 2 atoms of oxygen. This is not at variance with Dalton's Atomic theory and hence can stand.

Thus Gay Lussac's Law led to a distinction to be drawn between atoms and molecules.

The density of any gas with respect to Hydrogen is the ratio of the weight of a certain volume of that gas to the weight of the same volume of Hydrogen both measured at the same temperature and pressure. Let D be the density relative to Hydrogen of any gas. Then, by definition, we have

$$D=\frac{\text{wt. of } V \text{ vols. of the gas}}{\text{wt. of } V \text{ vols. of Hydrogen}} \quad \text{(under the same conditions of temp. and pressure).}$$

Let "n" be the number of molecules present in V vols. of the gas. Then, by Avogadro's hypothesis, we get

$$D=\frac{\text{wt. of ``}n\text{'' molecules of the gas}}{\text{wt. of ``}n\text{'' molecules of Hydrogen}}$$

$$=\frac{n\times\text{wt. of 1 molecule of the gas}}{n\times\text{wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 2 atoms of Hydrogen}}$$ (since Hydrogen molecule is diatomic as proved from Avogadro's hypothesis).

$$=\frac{\text{wt. of 1 molecule of the gas}}{2\times\text{wt. of 1 atom of Hydrogen}}$$

Hence, $$2\times D=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 atom of Hydrogen}}$$

= Molecular wt. of the gas (by definition).

or $$D\text{ (of any gas)}=\frac{\text{molecular wt. of the gas}}{2}.$$

Thus it is seen that density of any gas is half its own molecular weight.

Q. 2. *How was fluorine isolated? Give a neat sketch of the apparatus used. Compare its properties with those of chlorine.*

Ans. **Preparation of Fluorine by Moissan's method.**—Fluorine is prepared by the electrolysis of a solution of potassium hydrogen fluoride, KF, HF, in anhydrous hydro-fluoric acid, HF. The apparatus consists of a *U*-tube made of an alloy of Platinum-Iridium provided with two side tubes and fitted with fluorspar stoppers. Two electrodes made also of Platinum-Iridium alloy and thickened at the bottom pass through these fluorspar stoppers. The whole apparatus is kept immersed in a bath of boiling methyl chloride at about —22°C. The *U*-tube is $\frac{2}{3}$rd filled up with the electrolyte, a solution of KF, HF in anhydrous HF. On passing the current through the electrolyte HF undergoes decomposition, H_2 being liberated at the cathode and Fluorine at the anode. The Fluorine is led through a spiral of Pt kept immersed in boiling methyl chloride to remove any HF vapour by condensation. The gas is next passed through a tube of Pt packed with NaF which removes the last trace of HF. Fluorine is collected in a Pt—vessel by the upward displacement of air.

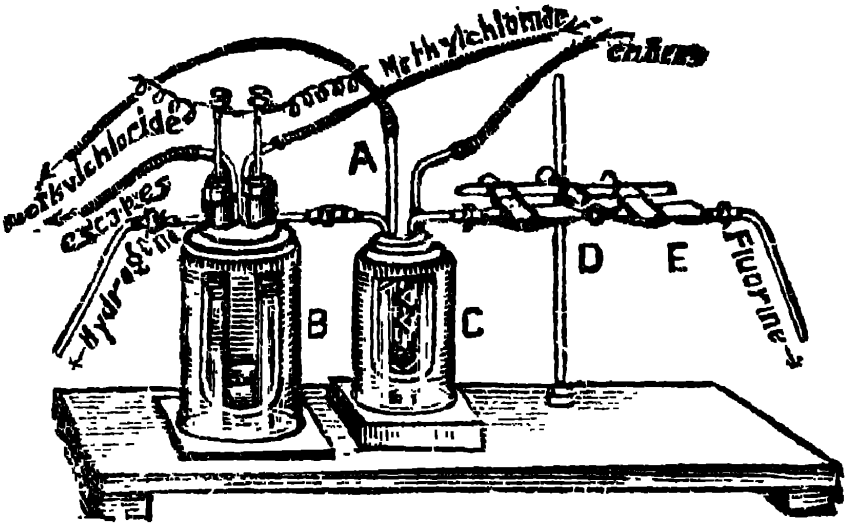


Fig. 22

Comparison of the properties of fluorine with those of chlorine :—

Physical Properties :—

Properties	*Fluorine*	*Chlorine*
(*a*) State of aggregation.	Gas	Gas
(*b*) Colour	Pale greenish yellow	Greenish yellow
(*c*) Odour	Irritating	Irritating and pungent.
(*d*) Heaviness or specific gravity.	Slightly heavier than air.	2½ times heavier than air.
(*e*) Solubility in water.	Decomposes water with evolution of ozonised oxygen and so solubility is not known.	Fairly soluble in water, giving what is called chlorine water.

Chemical Properties :—

Properties	*Flourine*	*Chlorine*
(1) Reaction with H_2.	Unites readily with H_2 even in the *dark* with explosion with the formation of HF which is stable.	Unites readily with H_2 in *direct sunlight* with explosion with the formation of HCl which is less stable than HF.
(2) Reaction with water.	Decomposes water with the formation of HF and evolution of ozonised oxygen :— $2F_2+2H_2O=4HF+O_2$ $3F_2+3H_2O=6HF+O_3$. These reactions take place at the ordinary temperature.	Decomposes water when the aqueous solution is kept exposed to sunlight with the formation of HCl which remains in solution and evolution of oxygen :— $2Cl_2+2H_2O=4HCl+O_2$. At 0°C. forms crystals of chlorine hydrate, $Cl_2 10H_2O$.
(3) Bleaching .tion.	Has destructive action on organic substances.	Readily bleaches vegetable colouring matter in presence of moisture.
(4) Chemical activity.	Most active : can liberate Cl from chlorides, Br from bromides and I from iodides.	Less active than fluorine : can liberate Br from bromides and I from iodides.
(5) Compounds with O_2 :—	Gives the oxide F_2O by direct combination. Another unstable oxide F_2O_2 is also recognised.	Forms several unstable oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7—all formed by indirect combination.
(6) Reactions with alkalies :—		
(*a*) Dilute and Cold.	With a 2% solution of NaOH, yields F_2O ; $2NaOH+2F_2 = 2NaF+F_2O+H_2O$.	With cold and dilute NaOH yields sodium chloride and sodium hypochlorite. $2NaOH+Cl_2= NaCl+NaClO+H_2O$.
(*b*) Concentrated and hot NaOH solution :	Evolves oxygen as gas and yields sodium fluoride.	Yields sodium chlorate and sodium chloride $6NaOH+3Cl_2= NaClO_3+5NaCl+3H_2O$.

Q. 3. *Describe how you would determine the composition of ammonia by volume as well as by weight.*

How is the molecular formula of the gas deduced from its composition ?

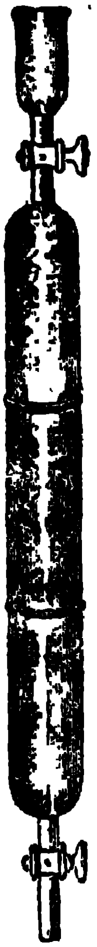


Fig. 23

Ans. The composition by volume of ammonia is determined by Hoffman's method.

The fact that ammonia is decomposed by chlorine producing N_2 and forming NH_4Cl is taken advantage of in this method to show the volumetric composition of ammonia.

A long glass tube fitted with a stop-cock at one end and a small dropping funnel at the other, is marked off into three equal divisions by India-rubber rings (Fig. 23). The tube is completely filled up with chlorine gas. A strong solution of ammonia is admitted into the tube drop by drop from the funnel until the reaction between the chlorine and ammonia ceases. Chlorine combines with the hydrogen of ammonia giving HCl and nitrogen is set free. HCl now reacts with excess of ammonia producing white fumes of NH_4Cl.

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

When an excess of ammonia has been added to ensure its complete conversion into NH_4Cl and N_2, the excess of ammonia is neutralised by adding dilute H_2SO_4 in excess. The stop-cock of the dropping funnel is now turned off, and the tube is placed in a tall jar containing water. The bottom stop-cock is now opened, when water rushes up and fills the tube nearly upto the second mark from the bottom. The level of water inside and outside the tube is now made the same, when the residual gas is found to occupy one-third of the vol. of chlorine taken. That the residual gas is Nitrogen is proved by the facts that it is inert, it does not readily combine with other elements and it is absorbed by strongly heated Magnesium.

We know that Hydrogen and Chlorine combine in equal volumes to form HCl gas. Therefore, 3 vols. of Chlorine taken in the tube, must have combined with 3 vols. of Hydrogen. These 3 vols. of Hydrogen must have come from Ammonia gas, which has simultaneously liberated 1 vol. of Nitrogen.

Thus, *ammonia is made up of one volume of Nitrogen combined with three volumes of Hydrogen.*

Let 1 vol. of Nitrogen contain "*n*" number of molecules. "*n*" molecules of Nitrogen combine with "3*n*" molecules of Hydrogen to form Ammonia (Avogadro) or 1 molecule of Nitrogen combines with 3 molecules of Hydrogen to form Ammonia.

But both Nitrogen and Hydrogen molecules are diatomic. ∴ 2 atoms of Nitrogen combine with 6 atoms of Hydrogen to give Ammonia.

$$\text{or, } \frac{\textit{No. of atoms of Nitrogen present in Ammonia}}{\textit{No. of atoms of Hydrogen present in Ammonia}}=\frac{2}{6}=\frac{1}{3}.$$

Hence the formula for Ammonia is $(NH_3)x$. Now the density of Ammonia determined experimentally is 8·5. ∴ the molecular wt. of Ammonia is 17. This tallies with the formula NH_3. Hence the molecular formula for Ammonia is NH_3, x being equal to 1.

Composition of ammonia by weight :—

Pure and *dry* ammonia gas is passed successively over heated black oxide of copper, CuO, placed covering the major portion of a long hard glass tube and then over red-hot metallic copper gauze placed at the other end of the same glass tube. The end where copper gauze is placed is connected with a weighed *U*-tube containing fused $CaCl_2$, where water produced by oxidation of ammonia is absorbed. The $CaCl_2$-tube in its turn is connected to a gas delivery tube, which is put under a gas-measuring tube filled with water and inverted over water in a trough. The copper oxide tube with copper and the $CaCl_2$-tube are weighed very accurately and then arranged as stated before. Ammonia gas is then passed for sometime till all the air from inside the whole apparatus is driven out and replaced by ammonia. The copper oxide tube is then strongly heated in a furnace. Ammonia is oxidised, and water and nitrogen are produced according to the equation

$$2NH_3+3CuO=3Cu+3H_2O+N_2.$$

Any oxide of nitrogen that might be formed is reduced by red-hot copper gauze to free nitrogen. Water is absorbed by $CaCl_2$ *U*-tube and nitrogen collects in the gas measuring tube by displacement of water. After the experiment is over, the gas measuring tube is closed with the thumb and dipped into a tall jar full of water and the level of water inside and outside the tube is made the same. The volume of nitrogen is then read off. The temperature of water in the tall jar is noted as also the barometric pressure. The copper oxide tube, when cooled to room temperature, is weighed again and the $CaCl_2$ *U*-tube is also weighed accurately.

The volume of nitrogen found is converted into a volume at N.T.P. after allowing for the aqueous tension at the temperature found and then multiplying this volume with 0·00126 we get the weight of nitrogen produced. The loss in weight of the copper oxide tube represents the weight of oxygen used up. The gain in weight of the $CaCl_2$ *U*-tube gives the weight of water produced. By taking the difference of the weight of water and the weight of oxygen used up, we get the weight of hydrogen. This weight of hydrogen is in combination with the weight of nitrogen calculated before in ammonia.

Deduction of formula from composition by weight of ammonia.—If the experiment be carefully performed, it is always found that 14 parts by weight of nitrogen is in combination with 3 parts by weight of hydrogen to produce ammonia. But 14 is the atomic weight of nitrogen and 3 can stand for 3 atoms of hydrogen, for the atomic weight of hydrogen is one. Hence the formula for ammonia is $(NH_3)x$, where x is an integer. Now the density of ammonia, as determined experimentally, is 8·5. Therefore, its molecular weight is 17. Hence $(14+3)x=17$ or $x=1$.

$\therefore$ the molecular formula of ammonia is NH_3.

Q. 4. *Describe experiments by which you can prove that both air and nitrous oxide contain the same constituents. What is the evidence that in one case the constituents are chemically combined, while in the other they merely form a mechanical mixture ?*

Ans. The same constituents of both air and nitrous oxide are oxygen and nitrogen. That air contains oxygen can be proved by exposing a jar of nitric oxide, NO, to air, when reddish brown fumes of NO_2 are produced, due to the combination of NO with oxygen of air. That nitrous oxide contains oxygen can be proved by passing nitrous oxide over heated metallic copper placed in a hard glass tube and collecting the issuing gas by displacement of water. The metallic copper is converted mainly into black oxide of copper by oxygen present in nitrous oxide and the gas collected can be proved to be nitrogen. That copper has been converted into oxide only can be shown by taking a quantity of it in a bulb-tube, weighing the bulb-tube along with this black substance, connecting the bulb-tube at one side with a pure hydrogen generator and the other end to a $CaCl_2$-tube with a guard tube, the two together being weighed ; pure hydrogen gas is then passed and the bulb-tube with the black particles are strongly heated. Water formed by this experiment collects in the $CaCl_2$-tube. The apparatus is then cooled in the atmosphere of hydrogen. The glass bulb is then detached and weighed. The $CaCl_2$-tube with the guard tube is then detached and weighed. The water formed as calculated from increase in weight of $CaCl_2$-tube is found to correspond to the loss in weight suffered by the bulb-tube calculated on the assumption that the loss in weight is due to removal of oxygen. This proves that the black substance is nothing but oxide of copper. That air also contains nitrogen can be proved by burning phosphorus in a closed volume of air and testing the residual gas which can be proved to be nitrogen by the usual tests.

In nitrous oxide, the elements nitrogen and oxygen are chemically combined because these two elements are present in definite proportions by weight and these two elements cannot be separated by easy mechanical means and mere blending of nitrogen and oxygen in the proportion in which they occur in nitrous oxide does not give rise to nitrous oxide. Moreover, the individual properties of nitrogen and oxygen are found to be absent in nitrous oxide.

Air is a mechanical mixture of nitrogen and oxygen because (*i*) these two elements are present in air in slightly varying proportions in different localities ; (*ii*) the two elements can be separated by easy mechanical means, *viz.* by diffusion or by solution in water. Air expelled from solution in water has a different composition from air which is originally dissolved in water. Fractional evaporation of liquid air causes separation of nitrogen and oxygen. (*iii*) When nitrogen and oxygen are mixed together in the same proportion as they occur in air, the mixture behaves in all respects as air. (*iv*) The individual properties of nitrogen and oxygen are all found to be present in air.

Q. 5. *How is potassium chlorate prepared? State its uses.*

Calculate the amount of potassium chlorate which on complete decomposition will yield just sufficient oxygen for the complete combustion of 1520 c.c. of a gaseous mixture, consisting of 20 per cent. methane and 80 per cent. carbon monoxide, at 27°C., and 750 mm. pressure.

$[K = 39{\cdot}0,\ Cl = 35{\cdot}5,\ O = 16{\cdot}0.]$

Ans. *Preparation of potassium chlorate,* $KClO_3$.—Chlorine is generated by heating MnO_2 with conc. HCl in a flask. The gas is washed with water and is then passed into a strong solution of KOH in water contained in a beaker by means of an inverted funnel. The beaker is taken away as soon as the liquid strongly smells of chlorine. The solution is then cooled, when crystals of $KClO_3$ separate out. The liquid is decanted off, the crystals are washed with a little cold water and $KClO_3$ re-crystallised from hot water.

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Uses of $KClO_3$.—Potassium chlorate is used in the laboratory for the preparation of oxygen; it is also used in the manufacture of matches, in preparation of explosive and pyrotechny. It has also medicinal use. As an oxidising agent, it is employed in chemical analysis.

Let V be the volume of the gaseous mixture at N. T. P.

Then by Boyle's and Charles' laws, we have,

$$\frac{1520 \times 750}{273 + 27} = \frac{V \times 760}{273},$$

whence $V = \dfrac{1520 \times 750 \times 273}{300 \times 760}$ c.c.

$= 1366$ c.c.

Since the gaseous mixture contains 20 per cent. methane, therefore, the volume of methane present $= \dfrac{20}{100} \times 1366$ c.c.

$= 273{\cdot}2$ c.c. at N.T.P.

Similarly, the volume of carbon monoxide present in the gaseous mixture $=\frac{80}{100}\times 1366$ c.c. $=1092{\cdot}8$ c.c. at N.T.P.

Now from the equations,

$$CH_4+2O_2=CO_2+2H_2O$$
1 vol. 2 vols.
$$2CO+O_2=2CO_2$$
2 vols. 1 vol.

We know that,

1 vol. of methane requires 2 vols. of oxygen for complete combustion and 2 vols. of carbon monoxide require 1 vol. of oxygen for complete combustion.

Therefore, 273·2 c.c. of methane at N.T.P. will require for complete combustion 546·4 c.c. of oxygen at N.T.P. and 1092·8 c.c. of carbon monoxide at N.T.P. will require for complete combustion 546·4 c.c. of oxygen at N.T.P. Hence, the total volume of oxygen required for complete combustion = 1092·8 c.c. at N.T.P.

Then, from the equation,

$$\underset{2\times 122{\cdot}5}{2KClO_3}=2KCl+\underset{3\times 32}{3O_2}$$

We know that 3 × 32 grams of oxygen can be obtained from 2 × 122·5 grams of potassium chlorate; that is, 3 × 22·4 litres of oxygen at N.T.P. can be obtained from 3 × 122·5 grams of potassium chlorate, since molecular weight of any gas, expressed in grams, occupies 22·4 litres at N.T.P. Hence 1092·8 c.c. of oxygen at N.T.P. can be obtained from $\frac{2\times 122{\cdot}5}{3\times 22400}\times 1092{\cdot}8$ grams, or 3·982 grams of $KClO_3$.

Q. 6. *How would you remove small quantities of (a) nitric oxide from nitrous oxide, (b) hydrogen chloride from chlorine, (c) water from ammonia, (d) chlorine from oxygen, (e) sulphuretted hydrogen from hydrogen and (f) bromine vapour from hydrobromic acid gas?*

Explain in each case the action of the reagent you would use giving equation.

Ans. (*a*) A cold solution of ferrous sulphate is taken and the gas mixture is bubbled through it. Nitric oxide is absorbed by ferrous sulphate solution, giving a brown solution containing the compound, $FeSO_4$, NO. Nitrous oxide also dissolves in water present in the solution till it is saturated and then it escapes free from nitric oxide and can be collected as usual over warm water.

$$FeSO_4 + NO = FeSO_4 . NO.$$

(*b*) The gas mixture is to be bubbled through cold water, first both hydrogen chloride and chlorine dissolve in water till water becomes saturated with chlorine. Hydrogen chloride is more soluble than chlorine and so it dissolves completely in water, chlorine escapes in the pure state and can be collected by displacement of brine, free from hydrogen chloride.

(*c*) Ammonia containing water is passed through a lime tower containing quicklime. Water is absorbed by CaO with the formation of $Ca(OH)_2$.

$$CaO + H_2O = Ca(OH)_2.$$

Dry ammonia will come out of the lime-tower and can be collected by displacement of mercury.

(*d*) Oxygen containing chlorine is to be passed through a solution of NaOH. Chlorine will be absorbed by NaOH solution producing sodium hypochlorite and sodium chloride. Oxygen coming out in the pure state can be collected by displacement of water.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

(*e*) Hydrogen containing sulphuretted hydrogen is to be bubbled through a solution of lead nitrate. H_2S will be absorbed with the precipitation of lead sulphide and hydrogen will be coming out free from H_2S and collected by displacement of water. $Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$.

(*f*) Bromine vapour can be removed from hydro-bromic acid gas by passing the mixture through a *U*-tube containing glass beads and moist red phosphorus. Moist red phosphorus reacts with bromine forming HBr and phosphorous and phosphoric acids. Hydrobromic acid gas escapes from the *U*-tube in the pure state and can be collected by upward displacement of of air.

$P+3Br=PBr_3$ $PBr_3+3H_2O=3HBr+H_3PO_3.$
$P+5Br=PBr_5$ $PBr_5+4H_2O=5HBr+H_3PO_4.$

Q. 7. *Describe without entering into details, an example of isolating metals from their ores by each of the following processes :—*

(*a*) *The reduction of their oxides with carbon or carbon monoxide.*

(*b*) *Self-reduction of their sulphides.*

(*c*) *Electrolysis of their compounds.*

Give a short account of the general properties of metals.

Ans. (*a*) By preliminary roasting of the common ores of zinc (zinc blende, ZnS, or Zincite, $ZnCO_3$) we can get zinc oxide, ZnO.

$$2ZnS+3O_2=2ZnO+2SO_2$$
$$ZnCO_3=ZnO+CO_2.$$

The oxide is then thoroughly mixed with carbon in the form of powdered coal or anthracite and the mixture heated to redness in cylindrical retorts made of fire-clay with the help of gaseous fuels. The oxide is thereby reduced to metallic zinc,

$$ZnO+C=Zn+CO.$$

Ferric oxide is obtained by preliminary calcination of ores (either red haematite, Fe_2O_3, or brown haematite, $2Fe_2O_3$, $3H_2O$ or spathic iron ore, $FeCO_3$). This ferric oxide is fed into a blast furnace along with coke and limestone and a blast of hot air is passed in through tuyeres. Carbon of coke first burns to carbon dioxide but is reduced by the layer of red-hot coke in its upward passage to carbon monoxide. Ferric oxide is reduced inside the blast furnace partly by carbon of coke and partly by carbon monoxide.

$$C+O_2=CO_2\ ;\ CO_2+C=2CO.$$
$$Fe_2O_3+3C=2Fe+3CO.$$
$$Fe_2O_3+3CO=2Fe+3CO_2.$$

(*b*) Lead is extracted from galena, PbS, by the process of self-reduction of this sulphide. Galena is first carefully roasted in a reverberatory furnace when it is converted partially into lead oxide and partially into lead sulphate while a portion of galena remains as such.

$$2PbS+3O_2=2PbO+2SO_2$$
$$PbS+2O_2=PbSO_4.$$

A little quantity of quicklime is then added to the mixed oxide, sulphate and sulphide and the temperature of the furnace is then raised to bright red-heat by closing the doors and windows of the furnace, when reaction takes place between oxide and sulphide, and sulphate and sulphide with the production of metallic lead and sulphur dioxide.

$$2PbO + PbS = 3Pb + SO_2.$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

(*c*) Sodium can be prepared by the electrolysis of fused sodium chloride and calcium can be obtained by the electrolysis of fused calcium chloride. In case of electrolysis of fused calcium chloride taken in a graphite crucible which is made the anode, the cathode being an iron rod kept dipped just below the surface of fused $CaCl_2$, calcium is liberated at the cathode and chlorine at the anode.

General properties of metals :—

Metals are elements which are mostly solids, only exceptions being mercury which is liquid at ordinary temperatures. They possess a characteristic lustre in the solid state or in the fused condition. In a very finely-divided state most metals appear black. Metals are generally found to possess malleability, ductility and tenacity. They are also characterised by their power of conducting heat and electricity.

Metals generally possess a high specific gravity, with some exceptions. Metals with a sp. gr. less than 5 are called *light* metals which include metals like Na, K, Mg, Al, etc., and those with sp. gr. higher than 5 are known as *heavy* metals. Metals in the fused state dissolve one another, producing mixtures or compounds which are known as *alloys.*

Chemical :

Metals combine with oxygen, either at ordinary temperature or when heated, forming their oxides. The oxides are mostly basic, but some are amphoteric like zinc oxide, aluminium oxide, etc. Metals generally displace hydrogen from an acid with the formation of their corresponding salts. Metals like gold, platinum, etc. are called noble metals and these do not readily combine with oxygen, nor do they dissolve in ordinary single acids. Copper, mercury, zinc, iron, etc., do not give hydrogen with nitric acid but give rise to nitrogen, or oxides of nitrogen or ammonia under different conditions. Halogens readily combine with metals giving their halides.

Q. 8. *What is the difference in composition between cast iron, steel and wrought iron ? Describe their properties and uses.*

How is steel manufactured by the Bessemer's Process ? Explain the reactions that occur.

Given metallic iron, how would you prepare from it ferrous sulphate, ferric chloride and magnetic oxide of iron ?

Ans. Difference in composition between cast iron, steel and wrought iron is given in the following tablo along with their properties on a comparative basis :—

Properties	Cast Iron	Wıought Iron	Steel
Carbon content	2 – 5%	0·12 – 0·25%	0·25 – 1·5%
Impurities	Also impurities like Si, Mn, P, S etc. are present	Purest form of commercial iron	Intermediate in purity between cast iron and wrought iron
Hardness	Hard	Hard	Hard and soft
Malleability	Brittle	Malleable	Melleable and brittle
Appearance	Crystalline	Fibrous	Crystalline
Melting point	1200°C.	1500°C.	1300°—1400°C.
Tempering	Cannot be tempered	Cannot be tempered	Can be tempered
Magnetisation	Cannot be permanently magnetised	Cannot be permanently magnetised	Can be permanently magnetised

The difference in properties of the different forms of iron is due to the presence of different proportions of other elements, combined and uncombined, in iron.

Uses :

Cast iron is used for casting ornamental iron goods like railings as also for iron articles. It is also used for the manufacture of steel and wrought iron. *Steel* is used in the manufacture of railway lines, locomotives, joist, etc. ; in the manufacture of war implements, appliances used in husbandry surgical instruments, cutlery, etc. It is also used in preparing artificial magnets, watch springs, etc. *Wrought iron* is used in the preparation of cores of electromagnets, piano wires and wires for binding flowers.

Manufacture of Steel by Bessemer's Process :—

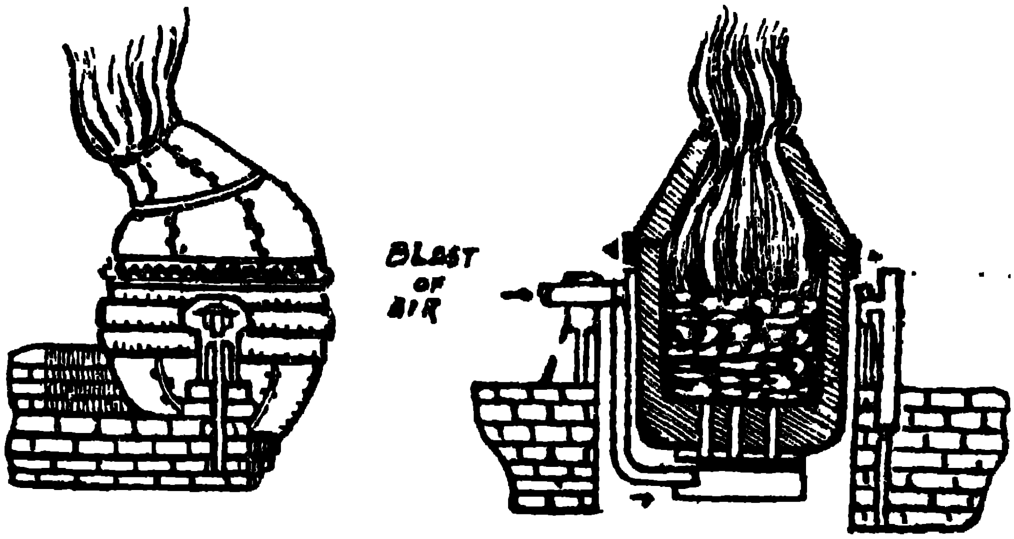


Fig. 24

At the present time steel is mostly prepared by the Bessemer's process. The process consists in oxidising the impurities present in cast iron, by blowing a blast of air through the molten metal. The operation is carried out in a large pear-shaped vessel made of wrought iron plates rivetted together, known as a *converter*. It is mounted on trunions, so that the converter can be tilted in any position, either vertical or horizontal, with its help. An air-chamber is fitted to the base, and through this air-chamber a powerful blast of air can be admitted. The converter is lined either with siliceous material (in *acid* Bessemer process) when the cast iron is free from phosphorus, or with burnt dolomite or magnesite (in *basic* Bessemer process) when phosphorus is present as impurity in cast iron.

The converter is first tilted into the horizontal position and a quantity of molten cast iron directly from the blast furnace is run in. The blast of air is then started and the converter immediately swung back into a vertical position. Within a very short time the whole of the impurities is burnt away. The completion of the operation is sharply marked by the sudden disappearance of the flame from the open mouth of the converter. The blast is stopped at this stage in the *acid* Bessemer process, but in the *basic* Bessemer process that blast is continued for a few minutes even after the dropping of the flame and it is stated that during this after-blow phosphorus is removed. The converter is then once more tilted into a horizontal position and an exact quantity of molten *Spiegel* (a mixture of C, Fe and Mn, containing about 20% Mn) is then added to recarburise the steel ; the blast of air is then turned on for a short time in order to mix the materials thoroughly. Next the contents are poured out into ladles. In case of phosphatic ores Spiegel is added after pouring the molten charge on to ladles.

The reactions that occur are :—Silicon is first attacked and oxidised to silica, SiO_2, which combines with FeO also formed producing a slag of ferrous silicate. Manganese is also oxidised and the oxide of manganese also passes into slag as manganese silicate. Iron is then attacked and the oxide of iron formed attacks carbon producing carbon monoxide. This carbon monoxide burns at the mouth of the converter with sparks from iron burning to a certain extent. In the basic process, phosphorus is oxidised at the end into P_2O_5 and this P_2O_5 combines with the MgO and CaO of the lining, forming phosphates which are removed as slag and used as manure. In the basic process some lime is also added along with the charge of cast iron in order to keep the slag basic.

Ferrous sulphate from metallic iron :

Metallic iron is dissolved in dilute sulphuric acid, the solution is filtered and the filtered solution is concentrated by evaporation out of contact with air.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

On crystallisation, crystals having the composition $FeSO_4$, $7H_2O$ separate out.

Ferric chloride from metallic iron :

Ferric chloride is known both in the *anhydrous* state ($FeCl_3$) and in the hydrated condition ($FeCl_3$, $6H_2O$).

Anhydrous ferric chloride can be obtained from metallic iron by passing a current of dry chlorine over heated (900°—1000°C.) metallic iron in the form of wires taken in a hard glass tube which is connected to a receiver. Black $FeCl_3$ collects inside the receiver.

$$2Fe + 3Cl_2 = Fe_2Cl_6.$$

Hydrated ferric chloride is prepared by dissolving metallic iron in aqua regia, filtering the solution and then evaporating the filtered solution to crystallisation when yellow crystals of hydrated ferric chloride separate out. $HNO_3 + 3HCl = 2H_2O + NOCl + \underset{\textit{nascent}}{2Cl}$

$$Fe + \underset{\textit{nascent}}{3Cl} = FeCl_3.$$

Magnetic oxide of iron (Fe_3O_4) from the metallic iron :

Metallic iron in the form of scraps is heated strongly in an iron tube and steam is passed over it. Hydrogen escapes as gas and magnetic oxide of iron formed remains in the iron tube from which it can be obtained by pouring it out after cooling.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

1944

SECOND PAPER

Q. 1. *What do you understand by a standard solution? How can you prepare a deci-normal solution of sulphuric acid?*

When one litre of a solution of silver nitrate was electrolysed for sometime, ·1259 grams of the metal were deposited on the cathode. 20 c.c. of the solution gave 1·677 grams of silver chloride *after electrolysis. Find the strength of the solution in terms of normality before and after the electrolysis.*

[Ag = 108, N = 14, Cl = 35·5]

Ans. The standard solution of a substance is a solution which contains a known weight of the substance dissolved in a known volume of it. Thus, the strength of a standard solution may be varied at will. Generally standard solutions are prepared in terms of normality, *i.e.*, in terms of fractions or multiples of equivalent wt. of the substance expressed in grams being taken and dissolved in a litre of the solution.

Preparation of $\frac{N}{10}$ H_2SO_4.

In order to prepare, say 1 litre, of a deci-normal $\left(\frac{N}{10}\right)$ solution of sulphuric acid, $\frac{1}{10}$th of its gram-equivalent is to be taken and dissolved in distilled water by adding the acid with stirring to water and the volume of the solution to be made up to 1 litre in a litre-measuring flask. Now sulphuric acid is a hygroscopic liquid and so it is not convenient to weigh it out accurately. Moreover, pure and concentrated sulphuric acid as supplied in the laboratory contains about 96% H_2SO_4 proper. Hence, the best procedure is to determine the sp. gr. of the sulphuric acid supplied with the help of a hydrometer and to find out the sulphuric acid content from a table. Suppose, the sp. gr. found is 1·8 and the sulphuric acid content as found from the table is 96% (app.). Now in order to prepare a deci-normal solution of sulphuric acid, we are to take 4·9 grams of H_2SO_4 proper, dissolve it in distilled water and the volume of the solution to be made upto 1 litre. (Equivalent weight of sulphuric acid is 49 grams). Now in order to get 4·9 grams of sulphuric acid proper, we are to take $\frac{4·9 \times 100}{96}$ or 5·104 grams of the sample supplied. Now, since the sp. gr. of the sample of sulphuric acid is 1·8, therefore, the volume of the sample to be taken is $\frac{5·104}{1·8} = 2·83$ c.c.

Actually 3 c.c. of the sample of sulphuric acid is measured out in a measuring pipette and added to distilled water contained in a beaker with constant stirring. The solution so produced is next transferred to a litre flask and the beaker is washed twice or thrice with distilled water and washings also transferred to the litre flask. The volume of the solution is then made upto 1 litre with distilled water and the solution thoroughly shaken. This solution will be a little stronger than deci-normal.

Then an exactly deci-normal solution of pure Na_2CO_3 (obtained by heating $NaHCO_3$) is prepared by weighing out as accurately as possible 5·3 grams of it, dissolving it in distilled water and making up the volume upto 1 litre with distilled water in a litre flask.

25 c.c. of this $\frac{N}{10}$ solution of Na_2CO_3 is taken out by means of a rinsed pipette into a clean procelain basin, two or three drops of Methyl orange (indicator) are added to it when it turns *yellow* and then the basin is placed below the burette. The acid solution prepared as stated above is taken in the burette in such a fashion that the upper meniscus of the acid coincides with the zero-mark of the burette. The acid is then added drop by drop with constant stirring with a glass rod till the solution turns *just pink*. The reading on the burette corresponding to the lowest edge of the meniscus is taken. Three such readings are taken each time, starting from the zero-mark of the burette coinciding with the lowest meniscus of the acid. The two consecutive readings must agree.

Let us suppose that 25 c.c. of $\frac{N}{10}$ Na_2CO_3 solution ≡ 20 c c. of the sulphuric acid solution.

In this case, therefore, 20 c.c. of the acid solution is to be diluted to 25 c.c. by addition of 5 c.c. of distilled water to give an exactly deci-normal solution.

That is, we are to measure out 800 c.c. of the acid solution prepared in a litre flask and dilute it with 200 c.c. of water to produce an exactly deci-normal solution, the solution being thoroughly shaken afterwards.

The molecular weight of silver chloride, AgCl is 108 + 35·5 or 143·5, in which silver present is 108. Therefore, in 1·677 grams of silver chloride, silver present is $\frac{1{\cdot}677 \times 108}{143{\cdot}5}$ grams or 1·2621 grams. And this amount of silver is present in 20 c.c. of the solution given after electrolysis. Hence, in 1000 c.c. of the solution, after electrolysis, the amount of silver present $= \frac{1{\cdot}2621 \times 1000}{20}$ grams $= 63{\cdot}105$ grams. Now normal solution of silver nitrate is that which will contain 108 grams (one gram-equivalent) of silver. Hence the normality of the solution after electrolysis $= \frac{63{\cdot}105}{108}$ N $= 0{\cdot}5843$N. Before electrolysis, since from a litre of the solution by electrolysis, 0·1259 gram of silver was deposited, the solution contained $(63{\cdot}105 + 0{\cdot}1259)$ or 63·2309 grams of silver.

Hence, before electrolysis, the normality of the solution $= \frac{63{\cdot}2309}{108}$ N $= 0{\cdot}58547$N.

Q. 2. *Name the sources from which silver can be obtained. Describe Parke's method for extraction of silver. Explain clearly the part played by zinc in the extraction. How is the metal obtained in pure condition ?*

From a soluble salt of silver, silver chloride is obtained as a precipitate. How can you convert it into the metal ?

How can a coating of silver be applied on the surface of a metal and glass ?

Briefly state the chemistry of photography.

Ans. Silver can be obtained from its sulphide and chloride ores and oftentimes from argentiferous galena. Important ores of silver from which silver is extracted are :—

(1) *Argentite* or *silver glance*, Ag_2S.
(2) *Copper-silver glance* or *Stromeyerite* $(Cu, Ag)_2S$.
(3) *Ruby Silver* or *Pyrargyrite*, $3Ag_2S, Sb_2S_3$.
(4) *Proustite*, $3Ag_2S, As_2S_3$.
(5) *Horn silver* or *Chlorargyrite*, AgCl.

Silver is recovered from lead obtained from argentiferous lead by Parke's method. When the argentiferous lead contains less than 1% of silver, it is concentrated with regard to silver by this method and then silver recovered from the enriched lead-silver alloy by the *Cupellation process.* In this method zinc is added in molten condition to molten argentiferous lead, when on stirring the mixture most of the silver goes to form an alloy with zinc. This alloy of zinc and silver, being lighter than lead, floats on the surface of molten lead. This alloy, on cooling, solidifies before lead begins to solidify. This solid alloy of zinc and silver is therefore readily skimmed off by perforated ladles. This zinc-silver alloy is then distilled from plumbago retorts, when zinc distils over, leaving behind a lead-silver alloy very rich in silver. This lead-silver alloy is cupelled, by being heated strongly on a cupel or test, made of bone-ash and set in the bed of a reverberatory furnace. A blast of air is projected on the alloy during heating. Lead is oxidised to lead monoxide by the blast of air and the molten oxide of lead (litharge) overflows by the force of the air-blast into iron pots placed beneath the cupel. Towards the end the thin film of litharge formed is absorbed completely by the porous cupel and the bright white silver surface suddenly shows itself, the phenomenon being known as the *flashing of silver.* The metallic silver so produced is then cooled and collected.

The action of zinc in Parke's process is to extract silver from lead and alloy with the silver extracted forming a lighter and less fusible alloy than the alloy of lead and silver. From this zinc-silver alloy, zinc can be easily separated by the process of distillation, zinc being the most volatile metal of the three : zinc, silver and lead.

On a large scale silver is refined by the Electrolytic process Pure silver nitrate is dissolved in distilled water in a vessel and 1% HNO_3 is added to it. A plate of pure silver is dipped in the solution and made the cathode, whereas the sample of the *impure* metal to be refined in the form of a cubic block is dipped in the same solution and made the anode. Electric current of requisite strength is then passed in with the help of a battery and the solution of silver nitrate containing nitric acid is thereby electrolysed. Pure silver is deposited on the cathode, and silver from the impure sample passes into solution. The impurities present in the sample like copper, gold, etc., either pass into solution or are deposited at the bottom of the vessel.

In order to convert the silver chloride precipitate into metallic silver, the precipitate of silver chloride is first dried and then mixed with pure Na_2CO_3. The mixture is taken inside a crucible made of pure lime and fused by application of heat, when a button of pure silver is obtained.

$$4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + 2CO_2 + O_2.$$

In order to apply a coating of silver on the surface of a metal, a solution of potassium silver cyanide, $KAg(CN)_2$, obtained by adding KCN in excess to silver nitrate solution, is taken in a vessel. The metal to be coated with silver is thoroughly cleaned and polished and is then dipped into that solution and made the cathode, while a piece of silver is dipped in the same solution and made the anode. An electric current of requisite strength is then passed from a battery when silver dissolves at the anode and is deposited at the cathode forming a coating. The metal with silver coating is taken out of the bath from time to time and brushed with a metal brush in order to produce a shining surface.

A coating of silver on glass surface can be given by placing the thoroughly cleaned piece of glass to be coated with silver inside a solution of silver nitrate taken in a flat basin, to which a solution of Rochelle salt is added when a white ppt. of silver tartrate is formed. This white ppt. is dissolved by addition of NH_4OH. The flat basin is then warmed by placing it in a bath of boiling water. A beautiful mirror of silver is formed on the glass surface.

Chemistry of Photography :

The photographic plate or film usually consists of particles of silver bromide, with other substances, embedded in gelatine. The parts of such a plate or film, on exposure to light, lose minute quantities of bromine (from the exposed part) which goes to combine with gelatine present, so that the action is no longer reversible. When exposure is over, the plate or film is taken out in a dark room, treated with a suitable developing agent, such as hydroquinone which reduces the affected portion of silver bromide to metallic silver. A visible image is thereby developed. The unexposed and unaffected silver bromide is removed by solution in a fixing bath containing a solution of sodium thiosulphate which dissolves out all unchanged AgBr. By this means the *negative* is produced where light and shade of the original object is reversed. In order to get a *positive* print the negative is placed in contact with a sensitive paper coated with AgBr as in the original film and the two together are exposed to light for a little time. By this means an invisible image is produced on the sensitive paper just opposite in character to the negative with respect to light and shade. This sensitive paper is then taken out and developed and fixed as before to give the final print.

During developing the reactions that take place, can be represented by the equation

$$C_6H_4(OH)_2 + 2AgBr = C_6H_4O_2 + 2Ag + 2HBr.$$

During fixing, the reaction is

$$3AgBr + 4Na_2S_2O_3 = Na_5[Ag_3(S_2O_2)_4] + 3NaBr.$$

The positive print is afterwards *toned* by dipping the print into a solution of either gold chloride or platinum chloride, whereby particles of silver are replaced by gold or platinum. This process is, however, optional.

Q. 3. *Describe the changes that take place when—*

(*a*) *a jet of burning hydrogen is introduced into a jar of chlorine,*

(*b*) *Ozone is led into a solution of ethylene or, ozone is introduced into a solution of potassium iodide,*

(*c*) *dry chlorine is passed over heated tin,*

(*d*) *hydrogen chloride is passed over heated aluminium,*

(*e*) *zinc dust is added to a solution of copper sulphate. What are the products formed in each of the above cases ? Represent the reactions by equation.*

Ans. (*a*) The jet of burning hydrogen continues to burn with evolution of white fumes of hydrogen chloride.

$$H_2 + Cl_2 = 2HCl.$$

(*b*) When ozone is led into ethylene, ozone is absorbed with the production of ethylene ozonide.

$$C_2H_4 + O_3 = C_2H_4O_3.$$

It is stated to be a solution of ethylene, and if water be present in that solution, then formaldehyde and hydrogen peroxide are produced.

$$C_2H_4O_3 + H_2O = \underset{\text{Formaldehdye}}{2CH_2O} + H_2O_2.$$

Or, when ozone is introduced into a solution of potassium iodide, iodine is liberated and ozone is reduced to oxygen, caustic potash being produced in solution.

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2.$$

(*c*) On passing dry chloride over heated tin, stannic chloride is formed which escapes as fumes and can be collected as a colourless fuming liquid in a receiver.

$$Sn + 2Cl_2 = SnCl_4.$$

(*d*) By passing hydrogen chloride over heated aluminium, aluminium chloride is formed and sublimes off along with hydrogen. The sublimate of anhydrous aluminium chloride can be collected in a suitable receiver.

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

(*e*) On adding zinc dust to a solution of copper sulphate, metallic copper is deposited and zinc passes into solution as zinc sulphate.

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

Q. 4. *You are supplied with a solid sample which contains calcium sulphate, potassium nitrate and iodine. How will you separate the ingredients and get them in pure condition !*

Write short notes on the methods involved in the principle of separation.

How will you show that calcium sulphate contains both calcium and sulphur and potassium nitrate contains nitrogen and oxygen ?

Ans. *The principle and process of separation of the ingredients of the mixture :*

Of the three constituents of the mixture, iodine can be converted into vapour by gentle heating, and the vapour is capable of being condensed into solid crystals of iodine by cooling. The process is called *sublimation*.

The mixture is taken in a porcelain basin and it is covered by another basin kept cool on its outer surface by a moistened filter paper. The basin is gently heated by being placed on a wire gauze over a tripod stand, iodine is vaporised and the vapour of iodine condenses as crystals inside the cooled covered basin in pure state. The heating is continued till all the iodine is removed in this fashion. In order to see whether all the iodine is removed or not, a little quantity of the solid is taken in a test tube, KI solution is added to it and then a little starch solution. If there be any blue coloration, the heating is to be continued till the residue is free from iodine.

The residue in the lower basin contains two substances : calcium sulphate and potassium nitrate. Of these two substances, KNO_3 is very soluble in water, whereas $CaSO_4$ is sparingly soluble.

So the residue, after cooling, is taken in a beaker, boiled with water and filtered. The residue is repeatedly washed with hot water, until the residue is completely free from KNO_3, as tested by the *ring test* for nitrate. The filter paper with the residue is then dried in an air oven to get pure calcium sulphate.

The filtrate contains potassium nitrate with a little $CaSO_4$ dissolved in it. From this mixture pure KNO_3 can be obtained by repeated fractional crystallisation, the first crop of crystals being discarded in each such process.

So sublimation separates iodine and filtration mechanically separates $CaSO_4$ as a residue, provided the pores of the filter paper be fine enough to retain the particles of $CaSO_4$.

Calcium sulphate.—The presence of calcium in calcium sulphate can be detected by flame test. A little of the salt is taken on the tip of a Pt-wire rinsed thoroughly with conc. HCl and after moistening it with conc. HCl it is held in a non-luminous Bunsen flame. A transient brick-red coloration is imparted to the flame, proving thereby that calcium is present in the salt.

To show that calcium sulphate contains sulphur, a little of it is mixed with charcoal powder and heated on charcoal in the reducing blow-pipe flame. The residue left is taken in a test tube and dilute HCl is added to it. Odour of H_2S is perceived and the gas evolved is found to turn lead acetate paper black. When the gas is burnt at the mouth of the test tube, a deposit of S is obtained. This sulphur must have come from calcium sulphate, since none of the reagents used contains sulphur.

Potassium nitrate.—On heating a little potassium nitrate in a hard glass test tube provided with a delivery tube, the gas evolved can be collected by displacement of water. The gas rekindles a glowing chip of wood, produces brown fumes with nitric oxide and is completely absorbed by alkaline pyrogallate. This proves that potassium nitrate contains oxygen.

A little of potassium nitrate is taken in a hard glass test tube provided with a cork through which passes a delivery tube. Potassium nitrate is fused by heating (m. p. 336°C.) and then a bit of sulphur is dropped on it, the cork being immediately replaced and the gas evolved being collected by displacement of water. That the gas collected is nitrogen can proved by the facts that it extinguishes a lighted taper, does not turn lime water milky and is absorbed by heated magnesium. This shows that potassium nitrate contains nitrogen. SO_2 is also evolved in this case but it dissolves in water over which the gas is collected.

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Q. 5. *How is acetylene prepared in the laboratory? Give a neat sketch of the apparatus you will use. Mention how the by-product of the preparation can be utilised.*

What changes will occur when acetylene is (a) lead into a jar of chlorine, (b) passed into an ammoniacal solution of copper sulphate and (c) passed into a dilute solution of sulphuric acid containing mercuric oxide in suspension at an elevated temperature?

Ans. Small lumps of calcium carbide are taken in a dry Erlenmeyer flask fitted with a dropping funnel and a delivery tube. Water is gradually dropped upon the lumps of calcium carbide from the dropping funnel, when acetylene gas is evolved. The gas can be collected by displacement of water.

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

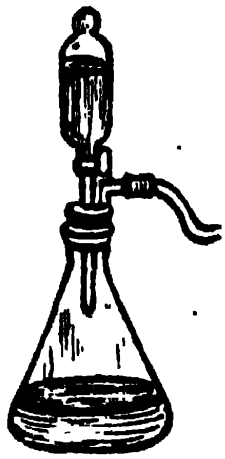


Fig. 25

The by-product of the preparation is slaked lime, $Ca(OH)_2$. It can be best utilised as a manure.

(*a*) When acetylene is led into a jar of chlorine, it at once bursts into flame giving HCl and carbon separates out.

$$C_2H_2 + Cl_2 = 2C + 2HCl.$$

But when chlorine is dissolved in S_2Cl_2 and acetylene led into that solution, additive compound, acetylene tetrachloride, is formed.

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4.$$

(*b*) When acetylene is passed into an ammonical solution of copper sulphate, a red precipitate of copper acetylide (Cu_2C_2, H_2O) is formed.

(*c*) When acetylene is passed into a dilute solution of sulphuric acid containing mercuric oxide in suspension at an elevated temperature, acetaldehyde, CH_3CHO, is produced.

$$C_2H_2 + H_2O = CH_3CHO.$$

Q. 6. *How is caustic soda manufactured from sodium chloride? Mention the uses this is put to.*

Discuss the action of carbon monoxide, carbon dioxide and iodine on this compound indicating the conditions. Represent the reactions by adequate equations.

Ans. Caustic soda is now-a-days manufactured by Castner-Kellner's modified process with the use of a diaphragm cell for separating caustic soda produced from evolved chlorine.

The apparatus consists of a rectangular vessel divided into two compartments (marked I and II in the adjoining figure) by a wooden partition which dips into a stream of Mercury running along the floor of the vessel from a reservoir R erected at a higher level, to the reservoir S. (See Fig. 26). Brine is placed in compartment marked I and a carbon rod is fitted therein to serve as anode. Water, containing a little caustic soda for making it conducting, is placed in compartment marked II, called the decomposer. A bunch of iron rods are placed in the decomposer to serve as cathode. The layer of mercury at the bottom of the vessel is electrically connected to the iron cathode. On passing electric current, Na is liberated in compartment I on the mercury functioning as cathode and forms sodium-amalgam. This sodium-amalgam is moved into the compartment II, the decomposer, by the running Mercury. There a portion of sodium-amalgam reacts with the water yielding NaOH, but major portion of sodium-amalgam reacts with the H-ions and OH-ions derived from the electrolysis of water, also yielding NaOH and liberating H_2 as gas. [Sodium-amalgam does not react with water in compartment I, because hydrogen cannot be liberated on mercury surface]. Nearly pure Mercury then runs down to reservoir S and is pumped back once more to R. Chlorine evolved at the anode escapes by the outlet shown in compartment I and Hydrogen liberated on the iron cathode in compartment II escapes by the outlet therein. The concentration of NaOH in compartment II is not allowed to rise above 20%. It is taken out from time to time, being replaced by water. NaOH solution is then evaporated till, on cooling, the whole mass solidifies. Thus solid caustic soda is produced. It is further melted down and then cast into sticks, pellets or balls.

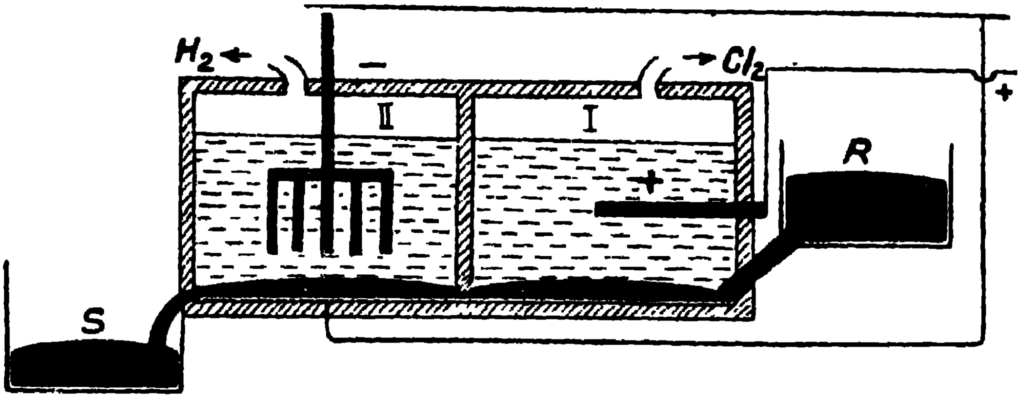


Fig. 26

$$2NaHg + 2H_2O = 2NaOH + H_2 + 2Hg$$
$$2Na + 2H^+ + 2(OH)^- = 2Na^+ + 2(OH)^- + 2H.$$

Two atoms of hydrogen liberated combine to form H_2 molecule and then gaseous hydrogen escapes from cathode compartment.

Uses of caustic soda.—Caustic soda is employed : (1) in the manufacture of soap, metallic sodium and many chemicals ; (2) in refining of petroleum ; (3) in making artificial silk ; (4) in the textile, and pulp, and paper industries ; (5) in reclaiming rubber, and (6) as a reagent in the laboratory.

When carbon monoxide is passed over heated caustic soda, or when carbon monoxide at 160°C. and under pressure is passed into NaOH solution, sodium formate, HCOONa, is formed.

$$NaOH + CO = HCOONa.$$

When carbon dioxide is passed into caustic soda solution, at first sodium carbonate is formed, but by passing carbon dioxide in excess, sodium bicarbonate separates out in the solid state.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

With cold and dilute NaOH solution, iodine produces sodium iodide and sodium hypoiodite, but sodium hypoiodite readily hydrolyses to hypoiodous acid.

$$2NaOH + I_2 = NaI + NaOI + H_2O$$
$$NaOI + H_2O = HOI + NaOH.$$

With hot and strong NaOH solution, iodine gives rise to sodium iodate and sodium iodide.

$$6NaOH + 3I_2 = NaIO_3 + 5NaI + 3H_2O.$$

Q. 7. *How are the following prepared :—*

(*a*) *Stannous chloride from tin.*

(*b*) *Blue vitriol from copper turnings.*

(*c*) *Corrosive sublimate from mercuric sulphate.*

(*d*) *Sodium hypophosphite from phosphorus ?*

Mention the names of the by-products, if any. Indicate the reactions by equation.

Ans. (*a*) *Anhydrous* stannous chloride can be obtained from tin by heating it in dry HCl gas. The *hydrated* stannous chloride $SnCl_2, 2H_2O$, can be prepared from tin by dissolving it in hot conc. hydrochloric acid.

$$Sn + 2HCl = SnCl_2 + H_2.$$

The solution, on evaporation, deposits crystals of $SnCl_2$, $2H_2O$ on cooling,

The by-product in this case is hydrogen.

(*b*) From copper turnings blue vitriol $CuSO_4$, $5H_2O$, can be prepared by heating the copper turnings with conc. H_2SO_4 till the evolution of sulphur dioxide ceases, cooling the solution so obtained, diluting with water and filtering, and then evaporating the filtrate to ·crystallisation. On cooling, crystals of blue vitriol are deposited.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Here the by-product is sulphur dioxide.

(*c*) *Mercuric chloride* (*Corrosive Sublimate*), $HgCl_2$, is prepared on a manufacturing scale by heating a mixture of mercuric sulphate and common salt in long-necked flat-bottomed flasks on a sand-bath.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

A little MnO_2 is added to prevent reduction of $HgCl_2$ formed to calomel by organic matter. After the reaction is over, the flasks are cooled and these flasks are then broken and the cake of mercuric chloride is removed. It is then dissolved in water by heating and purified by recrystallisation from water solution.

Here the by-product is sodium sulphate.

(*d*) Sodium hypophosphite can be obtained in solution by heating white phosphorus with 30% caustic soda solution when phosphine is evolved as a gas. Before heating, the air from the vessel in which the heating is carried out, is to be displaced by coal-gas, since phosphine evolved in this case is spontaneously inflammable in air.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Here phosphine is obtained as the by-product.

Q. 8. *How is borax obtained on a large scale? What changes take place when borax is heated alone? Write what you know about its use in qualitative chemical analysis.*

Starting with borax how can you prepare crystalline boric acid and boron?

Mention the uses of borax and boric acid.

Ans. Borax is now-a-days exclusively prepared from naturally-occurring calcium borates. Powdered *colemanite*, $Ca_2B_6O_{11}$, is boiled with Na_2CO_3 solution when insoluble $CaCO_3$ precipitates out. It is filtered and the filtrate evaporated to crystallisation and crystals separated by filtration.

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2.$$

The mother liquor is afterwards treated with CO_2 whereby further quantity of borax can be obtained from it by concentration and crystallisation.

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

When heated alone, borax, $Na_2B_4O_7$, $10H_2O$, loses water and swells into a voluminous spongy mass. On stronger heating it melts to a clear liquid consisting of the anhydrous salt, $Na_2B_4O_7$. On cooling in the absence of moisture this sets to a transparent glass. During solidification the anhydrous pyroborate decomposes into sodium metaborate and boron trioxide.

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3.$$

In qualitative chemical analysis, a Pt-wire, fused into a glass tube, is taken. A loop is made at the end of this Pt-wire. The loop is heated and dipped into a little powdered borax when a little quantity of borax adheres to the loop. The loop is again heated when borax first swells up and then melts into a colourless glass-like bead on the loop. A very small quantity of the salt to be tested is taken on the bead and the bead heated again first in the oxidising flame and then in the reducing flame of the Bunsen burner. The colour of the bead is then noted. The following colours of the bead are obtained with the salts of metals mentioned :—

Salt	*Colour of the borax-bead*	
	Oxidising flame	Reducing flame
Copper salts	Blue	Red (opaque)
Iron salts	Yellow	Bottle green
Manganese salts	Amethyst	Colourless

The reaction that takes place can be explained by taking the case of copper salt. At the temperature of the flame the copper salt decomposes into cupric oxide and this cupric oxide forms cupric borates with sodium metaborate and boron trioxide. These cupric borates are coloured blue. Hence the bead becomes blue in the oxidising flame with a copper salt. In the reducing flame, metallic copper is produced and so the bead becomes red and opaque. This red and opaque bead with copper salt in the reducing flame is best obtained, if the bead be moistened with a tin compound.

$$NaBO_2 + CuO = CuNaBO_3$$
$$CuO + B_2O_3 = Cu(BO_2)_2.$$

Crystalline boric acid from borax :

Strong hydrochloric acid is added in excess to a hot saturated solution of borax. Boric acid crystallises out on cooling the liquid.

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

Boron from borax :

Boric acid is first of all prepared from borax by the method described above. This boric acid, on strong heating, is converted into boron trioxide, B_2O_3.

$$4H_3BO_3 = 2B_2O_3 + 6H_2O.$$

The residue is then mixed with aluminium powder in a graphite crucible and heated to white heat. The molten mass is then allowed to cool when crystals of boron separate out. The regulus obtained is freed from excess of aluminium by prolonged treatment with hydrochloric acid.

$$B_2O_3 + 2Al = Al_2O_3 + 2B.$$

Uses of borax :

Borax is used (*i*) in the manufacture of glass, enamels, glazes, soaps, etc., (*ii*) in medicine, (*iii*) in laundry, (*iv*) as a flux and (*v*) in soldering.

Uses of boric acid :

Boric acid is used in medicine, as a preservative for milk and in manufacture of glass.

Q. 9. *Briefly discuss Mendeleef's Periodic Classification of elements. How has it systematised the study of Inorganic Chemistry ?*

What are your ideas about valency ?

Ans. In 1869 the Russian chemist Mendeleef discovered that when the elements are arranged in the order of their increasing Atomic weights, their properties vary from member to member in a definite way, but return more or less to the same value at fixed points in the series. He stated it as a law which is referred to as the **Periodic Law**, which runs thus :—

"*The physical and chemical properties of the elements and their compounds are periodic functions of their Atomic weights.*

Mendeleef arranged the elements in a table in the order of their increasing atomic weights. This table is known as the *Periodic Table* or the *Periodic system.* In the table the elements are found to be arranged in horizontal series in such a fashion that when elements with similar chemical properties are reached, they are arranged in the same vertical column. The horizontal series were called *periods* and the vertical columns were called *groups.* The original periodic table of Mendeleef has, however, undergone many modifications due to new discoveries. The present-day modified table in one form is reproduced below.

PERIODIC TABLE

(With **Atomic numbers** written above and **Atomic weights** written by the side of symbols).

Periods.	Group I R_2O RH A B	Group II R_2O_2 RH_2 A B	Group III R_2O_3 RH_3 A B	Group IV R_2O_4 RH_4 A B	Group V R_2O_5 RH_3 A B	Group VI R_2O_6 RH_2 A B	Group VII R_2O_7 RH A B	Group VIII R_2O_8 → forml. of oxides → forml. of hydrides A	Group O Or Gr. VIII B
1							1 H 1·008		2 He 4
2	3 Li 6·94	4 Be 9·02	5 B 10·82	6 C 12	7 N 14·01	8 O 16	9 F 19		10 Ne 20
3	11 Na 23	12 Mg 24·3	13 Al 26·97	14 Si 28·06	15 P 31·04	16 S 32	17 Cl 35·46		18 A 39·9
4	19 K 39·1 29 Cu 63·5	20 Ca 40 30 Zn 65·3	21 Sc 45·1 31 Ga 70	22 Ti 48·1 32 Ge 72·5	23 V 51 33 As 74·9	24 Cr 52 34 S 79·2	25 Mn 54·9 35 Br 79·9	26 27 28 Fe 55·8 Co 58·9 Ni 58·6	36 Kr 83·7
5	37 Rb 85·4 47 Ag 107·8	38 Sr 87·63 48 Cd 112	39 Y 88·9 49 In 114·8	40 Zr 91·20 50 Sn 119	41 Nb 92·9 51 Sb 121·76	42 Mo 96 52 Te 127·6	43 Ma 97 8 53 I 126·9	44 45 46 Ru 101·7 Rh 103 Pd 106	54 Xe 131
6	55 Cs 132·9 79 Au 197·2	56 Ba 137·37 80 Hg 200·6	57 La 139 * 58 - 71 Rare-earths 81 Tl 204	72 Hf 178·6 82 Pb 207·2	73 Ta 180·8 83 Bi 209	74 W 184 84 Po 210	75 Re 186·3 85 At 210	76 77 78 Os 191 Ir 193 Pt 195	86 Rn 222
7	87 Fr 223·1	88 Ra 226	89 Ac 227	90 Th 232·12	91 Pa 231	92 U 238·14			

* Rare-earths.—	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce,	Pr,	Nd,	Pm,	Sm,	Eu,	Gd,	Tb,	Dy,	Ho,	Er,	Tm,	Yb,	Ln

The periods are divided into *short* and *long*, according to the number of elements present in them. It is found from the table appended that the 1st period consists of only two elements, Hydrogen and Helium. The 2nd period contains 8 elements from Lithium to Neon and the 3rd period also consists of 8 elements from Sodium to Argon. The 2nd and 3rd periods are called *short periods*. Then comes the 4th period with 18 elements starting from Potassium to Krypton and similarly the 5th period consists of 18 elements starting from Rubidium and ending in Xenon. These 4th and 5th periods are known as *long periods*. The 6th period contains 32 elements, starting from Caesium and ending in Radon and comprising in itself all the fifteen rare-earth elements. This 6th period is called a *very long period* or a *monster period*. The 7th period is fragmentary and it consists of only six radio-active elements, of which the first one is an analogue of the alkali metals. The vertical groups now are nine in number, marked 0 (zero) to VIII. The group 0 includes the inert gases like Helium, Neon, Argon, etc., discovered long after the construction of the Periodic Table by Mendeleef in atmospheric air. These gases show no combining capacity and so their valency is zero. The group-number is found to correspond to the highest valency of the elements in the group with regard to oxygen.

By arranging the elements in the above fashion periodicity in both physical and chemical properties is at once apparent. Such physical properties as atomic volume (atomic weight ÷ specific gravity), melting-point, boiling-point, electrical conductivity, etc. when plotted against the atomic weight in a graph, perfectly periodic curves, showing waxing and waning, are obtained. In those graphs similar elements are found to occupy similar positions.

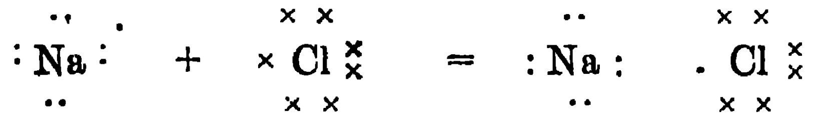
Similarly such typical chemical properties as valency and electro-chemical character of elements are found also to be periodic in nature.

Thus, the periodic arrangement has systematised the study of Inorganic chemisty by reducing the study of ninety-two different elements practically to that of nine Groups. Thus, we can form an idea of the properties of an element and its compounds by knowing the group it belongs to. Also a comparative study of the properties of different elements and their compounds, belonging to different groups, helps in understanding and remembering facts without encumbering the memory.

Valency of an element is defined as its combining capacity with other elements and is expressed as a number which indicates the number of hydrogen atoms or chlorine atoms with which one atom of the said element can combine.

Thus, considering such compounds as HCl, H_2O, NH_3, CH_4, we find that in hydrochloric acid, one atom of chlorine has combined with one atom of hydrogen ; in water, one atom of oxygen has combined with two atoms of hydrogen ; in ammonia, one atom of nitrogen has combined with three atoms of hydrogen, and in methane, one atom of carbon has combined with four atoms of hydrogen. Thus, the valency of chlorine is stated to be one, that of oxygen two, of nitrogen three, and of carbon four.

According to the present-day electronic theory of valency, developed as a necessary corollary of the electronic concept of matter, valency is considered as the tendency of the atom of an element either to lose or gain electrons from the outermost shell in the atomic core, so that the atom strives to attain a stable octet (a shell of eight electrons) in the outermost shell. Thus in the formation of sodium chloride, sodium atom loses one electron from the outermost shell (valency shell as it is called) and thus exposes the 8-electron penultimate shell, giving rise to sodium ion and chlorine atom gains that one electron, thus completing the 8-electron sheath, in the outermost shell :—



$$\overset{\cdot\cdot\;\cdot}{\underset{\cdot\cdot}{:\mathrm{Na}\,\vdots}} + \overset{\times\times}{\underset{\times\times}{\times\,\mathrm{Cl}\,\substack{\times\\\times}}} = \overset{\cdot\cdot}{\underset{\cdot\cdot}{:\mathrm{Na}:}}\quad \overset{\times\times}{\underset{\times\times}{\cdot\;\mathrm{Cl}\,\substack{\times\\\times}}}$$

(2, 8, 1) (2, 8, 7)

Only the penultimate and outermost shells of electrons of sodium atom (represented by dots) and chlorine atom (represented by ×) are shown in the above.

Hence the valency of sodium is one and of chlorine is also one, only one electron being transferred from sodium atom and only one electron being accepted by chlorine atom,

Valency at present is therefore regarded to be of electrical origin and the electrostatic force comes into operation in the exhibition of valency by atoms of elements.

1945

FIRST PAPER

Q. 1. *State Faraday's laws of electrolysis.*

A current of electricity is passed simultaneously through (a) silver nitrate solution, (b) copper sulphate solution and (c) water acidified with sulphuric acid. Calculate the amount of silver and copper that would be deposited by the time 124·7 c.c. of hydrogen at 27°C., and 750 mm. pressure are collected from the acidulated water.

[$Ag=108$; $Cu=64$.]

Ans. Faraday's laws of electrolysis are two in number.

Law I. The mass of an ion liberated during electrolysis is directly proportional to the strength of the current and to the time during which the current flows, *i.e.*, to the quantity of electricity flowing through the circuit.

Thus, if W be the mass in grams of an ion liberated, C the strength of the current in ampere and t the time in seconds during which the current flows, then $W \propto Ct$, or $W=ZCt$, where Z is a constant. Now when $C=1$ amp. and $t=1$ sec., then $W=Z=$mass of ion liberated by unit quantity of electricity. This quantity Z is called the *electro-chemical* equivalent of the substance.

Law II.—When the same quantity of electricity is passed through different electrolytes, the relative masses of different ions liberated are proportional to their chemical equivalents.

According to Faraday's second law of electrolysis, the masses of ions liberated at different electrodes by the same quantity of electricity are proportional to their chemical equivalents. So the amount of silver and copper that will be deposited by the same current flowing for the time in which the given amount of hydrogen is liberated will be obtained by multiplying the weight of hydrogen liberated by the equivalent weight of silver and copper respectively.

Now the equivalent wt. of silver $=108$, since it is monovalent and its at. wt. is given to be 108.

Also the equivalent wt. of copper in copper sulphate is $\frac{64}{2}=32$, since copper is bivalent in copper sulphate.

Now, we know that the weight of 1 c.c. of hydrogen at N.T.P. $=0{\cdot}00009$ gram.

Let the volume of hydrogen liberated at N.T.P, be V c.c.

Then by Boyle's and Charles' laws, we have

$$\frac{124{\cdot}7\times750}{273+27}=\frac{V\times760}{273},$$

$$\text{whence}\quad V=\frac{124{\cdot}7\times750\times273}{300\times760}\text{ c.c.}$$

$$=112\text{ c.c.}$$

The weight of hydrogen liberated, therefore, is equal to

$$112\times0{\cdot}00009\text{ gram.}$$
$$=0{\cdot}01008\text{ gram.}$$

Therefore, the weight of silver liberated

$$=0{\cdot}01008\times108\text{ grams}$$
$$=1{\cdot}08864\text{ grams.}$$

And the weight of copper deposited

$$=0{\cdot}01008\times32\text{ gram}$$
$$=0{\cdot}32256\text{ gram.}$$

Q. 2. *Explain the meaning of the term 'equivalent weight', illustrating your answer by reference to the equivalent weight of (a) zinc, (b) iron, (c) sodium carbonate.*

On heating in contact with tin, hydrogen sulphide (relative density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur from this.

Ans. The *equivalent weight* of an element is that weight of the element which combines with or displaces one part by weight of hydrogen or its equivalent (*i. e.*, 8 parts by weight of oxygen or 35·5 parts by weight of chlorine, etc.). It is also a mere number since it is a ratio expressed by the relation

$$\frac{\textit{weight of an element}}{\textit{weight of hydrogen displaced by it or combining with it}}.$$

It is known that 8 parts by weight of oxygen combine with 1 part by weight of hydrogen. Therefore 8 is the equivalent weight of oxygen.

(*a*) From actual experiment it is known that 32·65 parts by weight of zinc can liberate 1 part by wt. of hydrogen from sulphuric or hydrochloric acid.

Hence, from definition, 32·65 is the equivalent weight of zinc.

Also the valency of zinc is two and its atomic weight is 65·3.

Therefore, equivalent wt., being equal to $\frac{\text{atomic wt.}}{\text{valency}}$, in case of zinc, is $\frac{65·3}{2}=32·65$.

(*b*) In case of iron, it is known that 28 parts by weight of iron can displace 1 part by weight of hydrogen from hydrochloric or sulphuric acid, giving rise to ferrous salts in which the valency of iron is two.

Hence, from definition, 28 is the equivalent weight of iron in the ferrous state.

This also follows from the atomic weight of iron which is 56 and valency being two in the ferrous state,

Equivalent wt. of iron in ferrous state $=\frac{56}{2}=28$.

But it is also known from experiment that 18·66 parts by weight of iron combines with 35·5 parts by weight of chlorine to produce ferric chloride, where the valency of iron is three. Here, by definition, the equivalent weight of iron is 18·66. And this tallies with the result arrived at from the atomic weight of Iron (56) and its valency being three in this case, the equivalent wt. $=\frac{56}{3}=18·66$.

Thus, iron is found to possess two values for its equivalent weight depending upon its two valency states. This shows that equivalent weight of an element is not a constant quantity.

(*c*) In the case of a compound, the equivalent weight is that weight of it, which contains hydrogen-equivalent of the active element present it it. In the case of sodium carbonate, Na_2CO_3 (anhydrous) or $Na_2CO_3, 10H_2O$ (crystalline form) or Na_2CO_3, H_2O (the form obtained after keeping the crystals for some time exposed to air), the equivalent weight will be that weight which contains one equivalent of sodium, the active element present in it. The equivalent weight of sodium is 23. So, since Na_2CO_3, contains 46 parts by weight of sodium in 106 parts by weight of Na_2CO_3, therefore 53 will be its equivalent weight, since that amount will contain 23 parts by weight of sodium. Similarly, for the form $Na_2CO_3, 10H_2O$, the equivalent weight will be 143 whereas for the form Na_2CO_3, H_2O the equivalent weight will be 62.

From the result given, it is inferred that hydrogen sulphide contains its own volume of hydrogen. Let n be the number of molecules present in 1 vol. of hydrogen sulphide.

Then, since 1 vol. of hydrogen sulphide contains 1 vol. of hydrogen, therefore n molecules of hydrogen sulphide contain n molecules of hydrogen (Avogadro's hypothesis). Hence, 1 molecule of hydrogen sulphide contains 1 molecule, or 2 atoms of hydrogen, since hydrogen molecule is diatomic (deduction from Avogadro's hypothesis). Thus, the formula for hydrogen sulphide is H_2S_x, where x is an integer. Now, since the density of hydrogen sulphide is given to be 17, its molecular weight is $2 \times 17 = 34$ (deduction from Avogadro's hypothesis).

$$\text{Therefore} \quad 2 \times 1 + 32 \times x = 34$$
$$\text{or} \quad 32x = 32$$
$$\therefore x = 1.$$

Thus, the formula for hydrogen sulphide is H_2S. From this formula we know that 2 parts by weight of hydrogen has gone to combine with 32 parts by weight of sulphur to give hydrogen sulphide.

Hence, by definition, the equivalent weight of sulphur $= \frac{32}{2} = 16$.

Q. 3. *How is white phosphorus prepared? State the properties of allotropic forms of phosphorus. Describe, giving equations,* *the action of caustic soda solution on white phosphorus and of nitric acid on red phosphorus.*

Ans. Naturally occurring calcium phosphate is now-a-days utilised for getting white phosphorus. A mixture of calcium phosphate, sand and coke is fed through a feed-hopper into a closed electric furnace made of brick-work, provided with an outlet above for the gases and phosphorus vapour, a slag hole at the bottom and carbon electrodes a little above the bottom of the furnace between which an electric arc is struck, producing a very high temperature.

The silica of the sand reacts at the high temperature of the furnace with calcium phosphate producing calcium silicate and phosphorus pentoxide, P_2O_5.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

The vapour of P_2O_5 is then reduced by carbon and carbon monoxide is formed and phosphorus is set free.

$$P_2O_5 + 5C = 2P + 5CO.$$

Calcium silicate melts and sinks to the bottom from where it is run off as a slag through the slag hole. Phosphorus vapour and carbon monoxide escape through the outlet near the top and are passed into water where vapour of phosphprus condenses. Fresh mixture is introduced through the feed-hopper and the process is continuous.

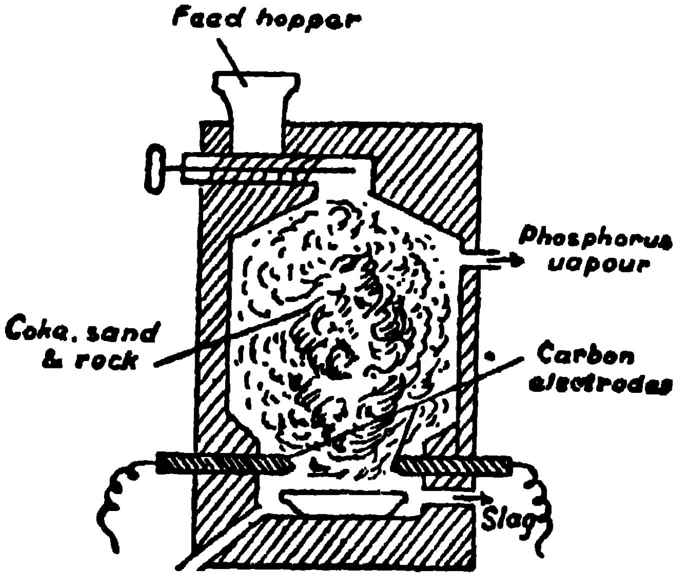


Fig. 27

The most important allotropic modifications of phosphorus are (*a*) White phosphorus and (*b*) Red phosphorus.

Properties of White Phosphorus :—

Physical—White phosphorus is almost colourless or slightly yellow, translucent, waxlike solid. It is soft enough to be cut with a knife. Its sp. gr. is 1·82. It melts at 44°C. It is very sparingly soluble in water, but dissolves readily in carbon disulphide. Phosphorus is very poisonous.

Chemical—When left exposed to moist air, white phosphorus undergoes spontaneous oxidation with the production of white fumes and phosphorescence which is visible in the dark. It takes fire in air at about 30°C. So it is always kept and cut, when to be used, under water. White phosphorus is very active chemically. It readily combines with the halogens at the ordinary temperature. When burnt in air, the main product is P_2O_5. It reduces H_2SO_4, HNO_3, $CuSO_4$, etc. It reacts when heated with NaOH or KOH sols. evolving PH_3.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Properties of Red Phosphorus :—

Red phosphorus is chocolate-red in colour. Its specific gravity is 2·2. It neither glows in the dark nor has any smell or taste. The melting point is 500° – 600°C. when heated under pressure. It does not dissolve in CS_2 nor in water. It is chemically less active than white phosphorus and is non-poisonous. Its ignition temperature in air is 240°C. It burns in chlorine gas when heated. It is not acted upon by NaOH solution. On strong heating red phosphorus can be vaporised and the vapour, on cooling, condenses into the white variety.

When white phosphorus is boiled with caustic soda solution in concentrated form, phosphine, PH_3, is evolved as gas and sodium hypophosphite is formed in solution.

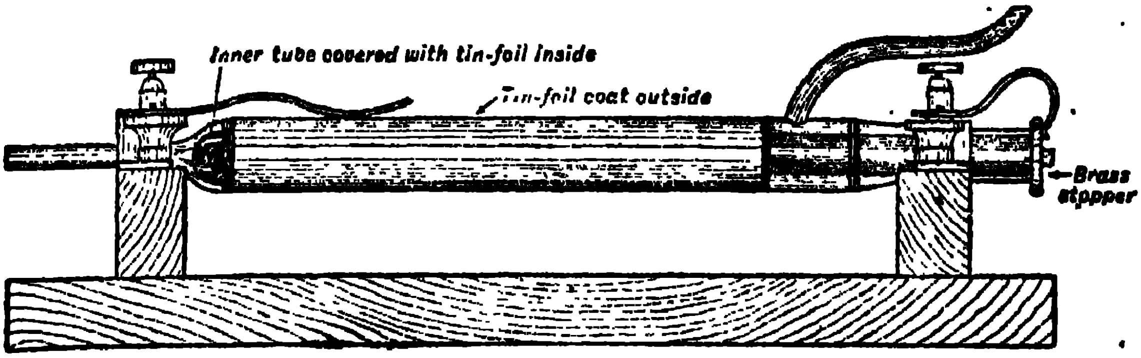
$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

When red phosphorus is boiled with concentrated nitric acid, orthophosphoric acid is formed in solution and oxides of nitrogen are evolved as brown fumes.

$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

Q. 4. *Describe how oxygen can be ozonised and illustrate with reference to three examples how ozonised oxygen differs from ordinary oxygen. How has the molecular formula of ozone been established ?*

Ans. Oxygen can be ozonised by subjecting it in dry state to the action of silent electric discharge in Siemen's ozoniser. This ozoniser consists of two concentric glass tubes, joined hermetically, without rubber or cork connections, the outer tube being coated on the outside and the inner tube on the inside with tin-foils. These tin-foils are connected with the two binding screws at the two ends, which in their turn are in connection with a Ruhmkorff's coil. Dry oxygen is passed through the annular space in slow steam and a series of silent electric discharge is passed. The gas coming out at the exit consists of a mixture of oxygen and ozone. $3O_2 = 2O_3$.



Siemens' ozoniser.

Fig. 28

(1) The gases are smelt. The one with fishy odour is ozonised oxygen, and the odourless one is simple oxygen.

(2) The gases are bubbled through acidified potassium iodide solution. The one which liberates iodine copiously and readily is ozonised oxygen, the other incapable of liberating iodine in that fashion is oxygen. The iodine liberated in the first case turns starch solution blue.

(3) Moist lead sulphide is taken on a filter paper and exposed to the gases. The one which turns black lead sulphide into white lead sulphate is ozonised oxygen, the other incapable of changing the colour of lead sulphide is oxygen.

Composition of Ozone and its Chemical formula :—

This may be proved experimentally in the following manner :

The contraction in volume on ozonising a known volume of oxygen is measured. The ozone is then absorbed by turpentine, and the further diminution in volume is noted. From these two data the composition of Ozone can be deduced and hence its molecular formula.

The apparatus for studying these volume changes is shown in the adjoining figure. It is devised by Newth.

It consists of two concentric glass tubes, the inner tube fitted into the outer tube by a ground glass joint. The inner tube which is nothing but an elongated hollow stopper contains dilute H_2SO_4 and the apparatus, previously filled with dry oxygen, is placed in a jar of water and crushed ice. Two platinum wires are dipped into the two liquids, one in dilute H_2SO_4 in the hollow stopper, and the other in the jar containing ice water and are connected with the terminals of an induction coil. The turpentine is contained in a little sealed thin

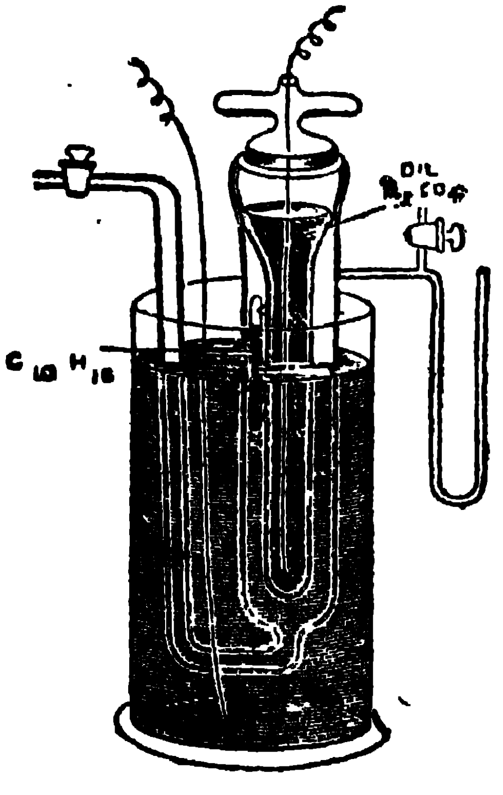


Fig. 29

glass tube, almost capillary in bore, which is held in position between four little projecting glass points upon the hollow stopper and the outer tube. A manometer, containing concentrated sulphuric acid coloured with indigo, is in communication with the apparatus. The levels are adjusted, and the oxygen is ozonized by passing the electric discharge. A contraction in the volume results. When sufficient contraction has taken place, the discharge is interrupted, the apparatus is allowed to cool and the contraction is read off on the manometer gauge. The hollow stopper is then twisted, so as to break the tube of turpentine, and after absorption of Ozone is complete, the further contraction is read off

Experimental Results :

1st contraction on ozonisation $= x$ c.c.
2nd contraction on absorption of
Ozone by turpentine $= 2x$ c.c.
$\therefore$ total diminution in volume of
Oxygen at the end of the expt. $= 3x$ c.c.
And the volume of Ozone formed $= 2x$ c.c.

Hence we conclude that 3 vols. of oxygen condense to give 2 volumes of Ozone.

Deduction of formula :—Let n be the number of molecules present in one volume of ozone. Then, by Avogadro's hypothesis, we get $3n$ molecules of oxygen condense into $2n$ molecules of Ozone.

Or, 3 molecules of oxygen condense into 2 molecules of Ozone. But 3 molecules of oxygen contain 6 atoms of oxygen (for oxygen molecule is diatomic). Thus 2 molecules of Ozone contain 6 atoms of oxygen. Hence its formula is O_3.

The molecular formula for Ozone has been confirmed by the determination of density of pure Ozone by Riesenfeld. It has a density of 24 and so the molecular wt. is 48, thus tallying with the molecular formula O_3.

Q. 5. *How is hydriodic acid prepared in the laboratory? Give a neat sketch of the apparatus used. Compare its properties with those of hydrochloric acid.*

Describe the changes that occur when (a) gaseous hydriodic acid is heated, (b) when its aqueous solution is treated successively with silver nitrate and ammonia, (c) when chlorine is passed into its solution followed by hydrogen sulphide. Give equations, whenever possible.

Ans. In the laboratory hydriodic acid is prepared by dropping water from a dropping funnel, fitted to a flask containing a mixture of red phosphorus and iodine. The flask is also provided with a delivery tube and the delivery tube is connected to a U-tube containing glass beads and moist red phosphorus. The flask is cooled by dipping it in water. Hydriodic acid gas mixed with iodine vapour is evolved in the flask and in passing through the U-tube containing moist red phosphorus iodine vapour is absorbed. The HI gas is then collected by upward displacement of air.

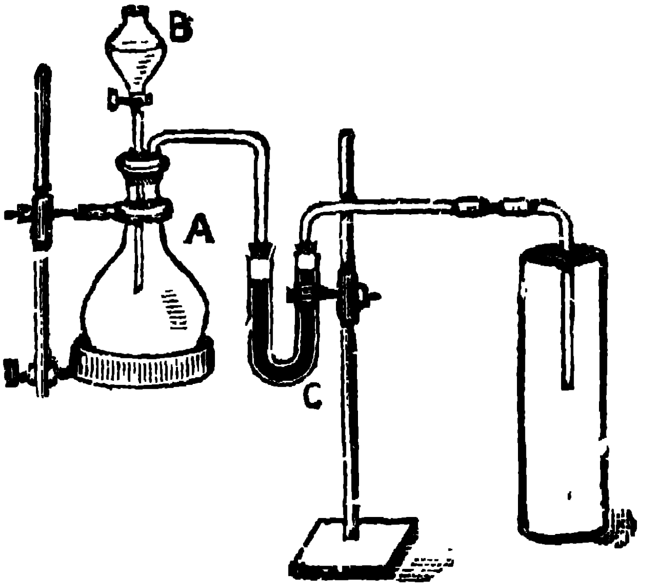


Fig. 30

At first phosphorus tri-iodide is formed, which is then decomposed by water forming phosphorous acid and hydriodic acid.

$$P + 3I = PI_3. \quad PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

When an aqueous solution of the acid is required, the delivery tube from the U-tube is connected to an inverted funnel, which in its turn is dipped into water contained in a beaker.

This arrangement is employed for preventing back suction due to extreme solubility of gas in water.

Comparison of the properties of HI with those of HCl.

Both HI and HCl are gaseous in character and both of them are soluble in water, giving strongly acid solutions. When exposed in water solution to air, HI turns brown due to liberation of iodine, but HCl solution fumes in air when concentrated but remains colourless. Boiled with conc. H_2SO_4, a concentrated solution of HI gives rise to violet vapours of I_2, whereas the concentrated solution of HCl gives rise to white fumes of hydrogen chloride. If silver nitrate solution be added to HI solution, a yellow ppt. of AgI, insoluble in HNO_3 as also in NH_4OH is obtained, whereas on adding $AgNO_3$ solution to HCl solution, a curdy white ppt. of AgCl, insoluble in HNO_3 but soluble in dil. NH_4OH is obtained. Chlorine water, when added to HI solution, liberates iodine which can be extracted with CS_2 giving a violet solution, but chlorine water has no action on HCl solution. HI solution behaves as a reducing agent on account of its easy oxidisability, whereas HCl has no such behaviour.

(*a*) When gaseous hydriodic acid is heated, it decomposes into its elements. **N. B.** In the presence of a catalyst like platinum, the decomposition and recombination of H_2 and I_2 takes place simultaneously, so that HI is stated to undergo dissociation.

$$2HI = H_2 + I_2.$$

(*b*) When the aqueous solution of hydriodic acid is treated with silver nitrate, a yellow precipitate of silver iodide is formed.

$$HI + AgNO_3 = AgI + HNO_3.$$

On subsequent addition of ammonia to the mixture, the yellow ppt. of AgI, being insoluble in NH_4OH, remains as such. The nitric acid liberated during the reaction is neutralised by NH_4OH. $HNO_3 + NH_4OH = NH_4NO_3 + H_2O$.

(*c*) When chlorine is passed into hydriodic acid solution, iodine is liberated.

$$2HI + Cl_2 = 2HCl + I_2.$$

On subsequent passage of hydrogen sulphide through the mixture, sulphur is precipitated and hydriodic acid is formed in solution.

$$H_2S + I_2 = 2HI + S.$$

If chlorine be passed in excess, the iodine liberated will be oxidised to iodic acid. The brown solution will turn colourless.

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

Then, on passage of H_2S, sulphur is precipitated no doubt but at the same time iodine is also set free. On continued passage of H_2S, of course, the sulphur alone will remain as a white or yellow ppt., and hydriodic acid will be formed in solution.

$$2HIO_3 + 5H_2S = I_2 + 6H_2O + 5S$$
$$I_2 + H_2S = 2HI + S.$$

Q. 6. *How would you obtain :*

(*a*) *Oxygen and chlorine from potassium chlorate,*
(*b*) *Nitrous oxide from nitre,*
(*c*) *Nitrogen from air,*
(*d*) *Mercury from corrosive sublimate,*
(*e*) *Anhydrous ferrous chloride from iron ?*

Explain the reactions involved and give equations.

Ans. (*a*) Potassium chlorate is mixed with manganese dioxide (MnO_2) to the extent of one-fifth of its weight and the mixture is taken in a hard-glass test-tube fitted with a cork and a delivery tube. The delivery tube is dipped under water in a pneumatic trough, over which a gas-jar full of water is inverted. The hard-glass test tube is next heated when a gas is evolved and is collected in the gas-jar by displacement of water. A solid residue is left in the test-tube.

$$\begin{array}{c} 2KClO_3 = 2KCl + 3O_2. \\ [+MnO_2] \quad [+MnO_2] \end{array}$$

The gas collected in the gas-jar is found to be capable of rekindling a glowing chip of wood, of producing brown fumes with nitric oxide and to be absorbed completely by alkaline pyrogallate, proving it to be oxygen.

The residue is heated till the evolution of oxygen completely ceases. Then it is taken in a flask fitted with a thistle-funnel and a delivery tube and is covered completely with concentrated sulphuric acid. The mixture is heated gently at first to see that no crackling sound is produced due to the presence of any undecomposed $KClO_3$. Then the mixture is heated somewhat strongly when a greenish-yellow gas is evolved. The gas is collected in a gas-jar by upward displacement of air.

$$2KCl + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + Cl_2 + 2H_2O.$$

That the gas is chlorine is proved by its greenish-yellow colour, peculiar pungent odour like that of bleaching powder and its capacity to turn starch-iodide paper blue.

(*b*) Nitre, KNO_3 is to be mixed with ammonium sulphate $(NH_4)_2SO_4$. The mixture is then taken in a round-bottomed flask provided with a cork through which passes a delivery tube. The mixture is then heated and the gas evolved is collected by displacement of hot water, since the gas is soluble in cold water. At first, by double decomposition ammonium nitrate is formed. This then decomposes giving nitrous oxide and water.

$$2KNO_3 + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4NO_3$$
$$NH_4NO_3 = N_2O + 2H_2O.$$

(*c*) From air, nitrogen can be obtained, admixed with the inert gases present in air, by passing air over heated metallic copper in the form of copper turnings taken in a hard glass tube and then collecting the gas escaping out. Oxygen of air combines with heated copper, leaving nitrogen free.

$$2Cu + O_2 = 2CuO.$$

When pure nitrogen is to be prepared from air, air is passed over an electric arc at a temperature of 3000°C. and the reaction mixture is rapidly cooled when NO is obtained in small amount. This reacts on cooling with oxygen still remaining in air, giving brown gas, NO_2. This is cooled in freezing mixture and collected in the liquid state. Other gases pass out, these being inert gases and remaining nitrogen and oxygen. This nitrogen peroxide is then vapourised by heating and passed over red-hot copper, when copper oxide is formed and nitrogen escapes and can be collected by displacement of mercury in a pure state.

$$N_2 + O_2 = 2NO$$
$$2NO + O_2 = 2NO_2$$
$$2NO_2 + 4Cu = 4CuO + N_2.$$

(*d*) Corrosive sublimate, $HgCl_2$, is mixed with soda-lime and the mixture taken in a glass test tube and heated. Small globules of mercury are found to be deposited in the upper cooler part of the test tube, giving a white mirror. These small globules are scratched with a glass rod and poured on a paper when bigger globules of mercury are obtained.

$$2HgCl_2 + 4NaOH = 2Hg + 4NaCl + 2H_2O + O_2.$$

(*e*) Anhydrous ferrous chloride can be obtained from iron, by heating a spiral of fine iron wire in a hard glass tube, connected on one side to a dry HCl generator and on the other to an empty bottle, and then passing a current of dry hydrogen chloride through the tube. Anhydrous ferrous chloride is deposited as colourless crystals inside the empty bottle out of contact with air.

$$Fe + 2HCl = FeCl_2 + H_2.$$

Q. 7. *Give an account of the manufacture of caustic soda from brine. Describe the changes which occur, writing equations where possible, when (a) caustic soda solution, (b) ammonia solution, is slowly added to solution of each of the substances—ferric chloride, aluminium chloride and copper sulphate.*

Ans. Caustic soda is manufactured from brine (sodium chloride solution) by electrolysis in a diaphragm cell. Nelson cell is now-a-days largely employed for the purpose. It consists of a rectangular steel tank, provided with outlets, a side tube for letting in steam and a tap at the bottom for taking out caustic soda solution formed in the tank. The cathode is in the form of a *U*-tube and is made of a perforated steel plate mounted inside the tank : it is lined inside with asbestos. This cathode divides the tank into two compartments : one, anode inside the U-shaped vessel and the cathode compartment outside

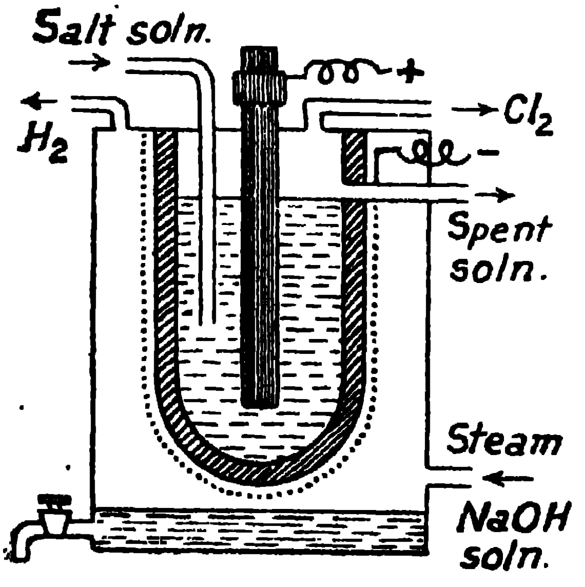


Fig. 31

it. The ends of the anode compartment are closed by cement. Brine is carefully purified and fed into the anode compartment in which a graphite rod is placed dipping in the brine. The graphite rod is connected to the positive pole of a battery and is thus made the anode ; the *U*-shaped steel vessel is connected with the negative pole of the same battery and serves as the cathode. An inlet pipe is inserted into the brine in the anode compartment through which purified sodium chloride solution can be fed in and there is also an outlet pipe set near the top of the *U*-shaped vessel in order to let out electrolysed brine. When current is put on, brine that gradually diffuses through the porous asbestos lining and reaches the cathode, undergoes electrolysis. Sodium, liberated at the cathode, is converted by reacting with water into NaOH ; chlorine liberated at the anode escapes by the outlet pipe set at the top. Hydrogen liberated in the cathode compartment is led off by the outlet-pipe set at its top. During electrolysis steam is blown into the cathode compartment to dissolve out the caustic soda formed at the cathode and thus prevent clogging of the diaphragm and to heat the cell, thereby reducing its electrical resistance. The following changes take place on passing the current :

$$2NaCl \rightleftharpoons 2Na^+ + 2Cl^- \text{ (in brine)}$$
$$2Na^+ \rightarrow 2Na$$
(at cathode)
$$2Cl^- \rightarrow 2Cl \rightarrow Cl_2 \text{ (gas at anode)}$$
(at anode)

Sodium atoms liberated at the cathode also react with steam, forming caustic soda and evolving hydrogen :

$$2Na + 2H_2O = 2NaOH + H_2$$
(gas in cathode compartment)

(*a*) When caustic soda solution is added to *ferric chloride* solution, brown ferric hydroxide is precipitated and sodium chloride is formed in solution.

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

(*b*) When ammonia solution containing ammonium hydroxide, is added to *ferric chloride* solution, brown ppt. of ferric hydroxide is formed as with NaOH, but ammonium chloride is formed here in solution.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$$

(*a*) When caustic soda solution is added to *aluminium chloride*, at first a white gelatinous ppt. of aluminium hydroxide is formed, but on addition of excess of caustic soda solution the ppt. of $Al(OH)_3$ dissolves, giving sodium aluminate.

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

(*b*) On addition of ammonia solution to *aluminium chloride* solution, the same white gelatinous ppt. of $Al(OH)_3$ is formed as with NaOH solution, but in this case the ppt. does not dissolve on addition of excess of ammonia solution. This is also because of the fact that the ppt. of $Al(OH)_3$ is insoluble in NH_4Cl which is also formed during the reaction.

$$AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl.$$

(*a*) When a solution of caustic soda is added to *copper sulphate* solution, a bluish white ppt. of copper hydroxide is formed. This copper hydroxide ppt. is insoluble in exces of caustic soda solution.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$

(*b*) When a solution of ammonia is added to copper sulphate solution, at first a bluish white ppt. of copper hydroxide is formed, but this precipitate dissolves to a deep blue solution of cuprammonium sulphate on addition of excess of ammonia solution.

$$CuSO_4 + 2NH_4OH = Cu(OH)_2 + (NH_4)_2SO_4$$
$$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O.$$

Q. 8. *Name the important ores of zinc. Describe the extraction of this metal and state its uses. Explain the action of sulphuric acid, nitric acid, sodium hydroxide and copper sulphate solution on zinc.*

Ans. The important ores of zinc are

(1) *Red zinc ore* or *zincite*, ZnO.

(2) *Franklinite.* (Zn, Fe)O, Fe_2O_3.

(3) *Calamine* or *Smithsonite*, $ZnCO_3$.

(4) *Zinc blende, black-jack* or *sphalerite*, ZnS.

The metallic zinc is obtained from its ores by the Carbon Reduction Process. When zinc blende is employed for getting the metal, the ore requires preliminary concentration on account of its being associated with galena, (PbS), quartz, sand, etc. For this purpose the crushed ore is placed in water to which a little oil and a little acid are added and the whole mixture is stirred up vigorously. ZnS rises to the surface and is removed therefrom. The impurities, like galena, sand, etc., collect at the bottom.

When calamine, $ZnCO_3$, is used for the extraction of the metal, no preliminary concentration is found to be necessary.

Purified zinc sulphide is next roasted carefully in a multiple hearth furnace in a current of air, whereby it is converted into zinc oxide, ZnO. Care is to be taken to see that the ore is completely converted into ZnO and not into $ZnSO_4$.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

In case of calamine, calcination will convert it into ZnO by elimination of carbon dioxide.

$$ZnCO_3 = ZnO + CO_2.$$

The oxide is next mixed thoroughly with an excess of powdered coal (or Anthracite) and the mixture is heated strongly in cylindrical fire-clay retorts by gaseous fuel to a temperature of 1300°—1400°C. The retorts are closed at one end and are fitted at the open end, after charging, with a clay tube which serves as a condenser for zinc-vapour. A large number of such retorts are arranged in rows in the furnace, slightly slanting towards the mouth. During heating zinc oxide is reduced to metallic zinc and carbon combines with the oxygen of zinc oxide giving carbon monoxide. If there be any CO_2 formed, it is reduced by excess of carbon at the high temperature to carbon monoxide ; this carbon monoxide formation is aimed at because if any CO_2 be formed, then that will oxidise the zinc vapour to zinc oxide. Carbon monoxide burns at the mouth of the clay tube with a blue flame. After a time, the flame becomes much more brilliant, indicating that the metal is coming out as vapour. Then a smaller condenser, made of Iron, known as *prolong*, is fitted to the end of each clay tube for complete condensation of Zn-vapour. A portion of zinc vapour condenses as liquid metal in the clay tube, and zinc mixed with a little zinc oxide condenses in the prolong. The molten zinc is taken out from time to time and cast into blocks.

$$ZnO + C = Zn + CO.$$

Uses of zinc.—Zinc is used for construction of electric cells like Daniell cell, for galvanising iron, in the preparation of alloys like brass, German silver, etc., pneumatic trough, gas holders, etc.

Pure zinc is scarcely acted upon by pure sulphuric acid, owing to the deposit of a thin film of hydrogen which protects the surface of the metal from corrosion by acid. The presence of small quantities of impurities, however, brings about the dissolution of the metal by sulphuric acid with the rapid evolution of hydrogen, due to some sort of galvanic couple being formed by zinc along with the impurities present in it.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Hot and concentrated H_2SO_4 attacks zinc giving off SO_2.

$$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O.$$

Zinc dissolves in moderately dil. HNO_3 giving N_2O ; with very dil. HNO_3 it gives NH_4NO_3, whereas conc. HNO_3 gives NO_2 with zinc.

$$4Zn + 10HNO_3 \text{ (moderately dilute)} = 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$4Zn + 10HNO_3 \text{ (dil.)} = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$Zn + 4HNO_3 \text{ (conc.)} = Zn(NO_2)_2 + 2H_2O + 2NO_2.$$

When heated with caustic soda solution, zinc dissolves with the formation of sodium zincate and evolution of hydrogen.

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Since zinc occurs above copper in the electro-chemical series, zinc displaces copper from copper sulphate solution, copper being precipitated as a red powder.

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

SECOND PAPER—1945

Q. 1. *5 grams of sulphur were completely burnt in pure oxygen. Calculate the volume of the product measured at 25°C. and 756 mm. pressure.*

This amount of the gaseous product was led into 75 c.c. of a solution of caustic soda, which then required another 75 c.c. of the same solution to show a neutral reaction. Calculate the strength of the caustic soda solution in terms of normality and also find out the total quantity of solid present in the neutral solution ($S=32$, $O=16$, $Na=23$, $H=1$).

Ans. From the equation

$$\underset{32}{S}+O_2=\underset{64}{SO_2}$$

we know that 32 grams of sulphur, on complete combustion, yield 64 grams of sulphur dioxide, that is, 22·4 litres of sulphur dioxide at N.T.P., since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P.

Therefore, 5 grams of sulphur on complete burning in pure oxygen, will give rise to $\frac{22{\cdot}4}{32}\times5$ litres of SO_2 at N.T.P. Let V be the volume of this SO_2 at 25°C. and 756 mm. pressure,

Then by Boyle's and Charles' Laws, we have

$$\frac{\frac{22{\cdot}4\times5}{32}\times760}{273}=\frac{V\times756}{273+25},$$

$$\text{whence}\quad V=\frac{22{\cdot}4\times5\times760\times298}{32\times273\times756}\text{ litres}$$

$$=3{\cdot}841\text{ litres.}$$

Again, the gaseous product from the burning of 5 grams of sulphur completely neutralised the caustic soda present in (75 + 75) or 150 c.c. of the solution of caustic soda used.

Now, from the equations, $\underset{32}{S}+O_2=\underset{64}{SO_2}$

$$\underset{64}{SO_2}+\underset{2\times40}{2NaOH}=\underset{\substack{2\times23+32+3\times16\\ \text{or,}\\ 126}}{Na_2SO_3}+H_2O$$

we know that 32 grams of S, on complete combustion, give rise to as much SO_2 as can neutralise 2×40 grams of NaOH and produce 126 grams of sodium sulphite.

Therefore 5 grams of S, on complete combustion, will give rise to as much SO_2 as will neutralise $\frac{2 \times 40}{32} \times 5$ grams or 12·5 grams of NaOH and produce $\frac{126}{32} \times 5$ grams, or 19·6875 grams of Na_2SO_3.

Hence 12·5 grams of NaOH were present in 150 c.c. of the solution of caustic soda provided. Therefore, 1000 c.c. of the caustic soda solution used contained $\frac{12·5 \times 1000}{150}$ grams or $\frac{250}{3}$ grams of NaOH. Now, the normal solution (N) of caustic soda contains 40 grams of NaOH per litre of solution. Therefore, the strength of caustic soda solution supplied $= \frac{\frac{250}{3}}{40}$ (N) $= \frac{250}{120}$ (N) $= 2·083$ (N). Also, the total quantity of solid sodium sulphite present in the neutral solution (which could be recovered on evaporating the solution to dryness) $= 19·6875$ grams.

Q. 2. *Write explanatory notes on :—*

(*a*) *Ionisation* ; (*b*) *Dissociation* ; (*c*) *Neutralisation* ; *and* (*d*) *Avogadro's Hypothesis.*

Illustrate your answers with suitable examples.

Ans. (*a*) When acids, bases and salts are dissolved in water, they are said to break down into electrically charged particles called ions. This breaking-up into electrically charged particles of the above class of substances on being dissolved in water is known as *ionisation.* This is a reversible phenomenon.

Thus, nitric acid in water solution is stated to break up as follows :—

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

Also

$$KOH \rightleftharpoons K^+ + OH^-$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{=}$$

The breaking down into ions and recombination of ions to form undissociated compound go on simultaneously until an equilibrium condition is set up, but water being removed the unionised compound is got back. This phenomenon is also called *electrolytic dissociation,*

(*b*) When a chemical compound decomposes under the influence of heat and the products are capable of recombining to form the original compound under exactly the same condition, the process is said to be one of dissociation.

Thus, when ammonium chloride, NH_4Cl, is heated in a closed vessel, it breaks up into NH_3 and HCl but NH_3 and HCl recombine to form NH_4Cl under similar conditions until a dynamic equilibrium is set up.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Similarly, in case of PCl_5,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

or, of I_2, $I_2 \rightleftharpoons I + I$.

This phenomenon is also called *thermal dissociation.*

(*c*) The process of neutralisation of an acid by a base consists in the combination of the hydrogen present in an acid with the oxygen or hydroxyl group present in a base, producing water and salt, when the two are brought together.

Thus,

$$\underset{\text{Acid}}{HCl} + \underset{\text{base}}{KOH} = \underset{\text{salt}}{KCl} + \underset{\text{water.}}{H_2O}.$$

$$\underset{\text{Acid}}{H_2SO_4} + \underset{\text{base}}{CaO} = \underset{\text{salt}}{CaSO_4} + \underset{\text{water.}}{H_2O}.$$

In the light of the ionic theory, neutralisation of an acid by a base consists in the combination of the H^+ ion of the acid with the $(OH)^-$ ion of the alkali (a strong base) with the formation of undissociated water.

Thus,

$$\begin{aligned} HCl + KOH &= H^+ + Cl^- + K^+ + (OH)^- \\ &= \underbrace{K^+ + Cl^-}_{\text{Dissociated salt}} + \underset{\text{Undissociated water}}{H_2O} \end{aligned}$$

(*d*) Avogadro's hypothesis states that *equal volumes of all gases and vapours (elementary or compound) under the same condi-*

tions of temperature and pressure contain the same number of molecules.

Thus, when at a fixed temperature and pressure a vessel is successively filled with different gases and vapours, either elementary or compound, like oxygen, chlorine, hydrogen chloride or steam, the vessel will contain exactly the same number of molecules of those different gases and vapour.

The number of molecules in a gram-molecule of all gases, which occupies 22·4 litres at N.T.P., is the same and is called *Avogadro Number.* It has a value $6·06 \times 10^{23}$.

Q. 3. *We get fairly extensive deposit of Bauxite in India, but no cryolite, although sodium fluoride and aluminium fluoride are available. Can you suggest a method for the preparation of the metal in this country ? Give a clean sketch of the apparatus that you may require for its manufacture and enumerate the conditions you will adhere to.*

Discuss the changes that you will observe when (a) nitric acid is added to pure aluminium, (b) hydrogen chloride is passed over the heated metal and (c) aluminium is dipped into a solution of aluminium chloride.

Ans. Cryolite is essentially necessary in the manufacture of aluminium, since the electrolytic bath in this case is of fused cryolite, in which the electrolyte, pure fused Al_2O_3, is dissolved. Now, the composition of cryolite is represented by the formula, AlF_3, 3NaF. So from sodium fluoride and aluminium fluoride available the electrolytic bath can be prepared by fusing together a mixture of the two, taken in the proportion of 1 molecule (84 parts by weight) of AlF_3 and 3 molecules (126 parts by weight) of NaF in the vessel described below and this fused mass will dissolve purified bauxite and serve for every purpose the requirements of cryolite.

The metal Aluminium is extracted exclusively from bauxite, Al_2O_3, $2H_2O$. But since this contains iron, it is first purified.

Purification of bauxite :—

Bauxite is fused with Na_2CO_3 or NaOH :—

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2.$$

The cold mass is extracted with water.

Or, bauxite is first roasted at a low temperature to convert

FeO into Fe_2O_3 and then it is digested with a solution of NaOH in iron vessels under pressure and at a temp. of 150°C. :

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O.$$

The alumina is precipitated from the solution obtained after the removal of insoluble impurities either (*i*) by passing CO_2 at 50° - 60°C.

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3$$

Or, (*ii*) by digesting with some freshly precipitated $Al(OH)_3$ with constant agitation when nearly all the $Al(OH)_3$ comes down as an amorphous precipitate. (—*Baeyer's Process*).

In either case the ppt. is washed, dried and ignited at 1000°C., when pure Al_2O_3 (98·8%) is obtained.

Extraction of Aluminium from purified bauxite by electrolysis :—Purified bauxite is now dissolved in a bath of molten cryolite and electrolysed in an electric furnace. The furnace consists of a rectangular iron box which is lined with fire-bricks and then with blocks of gas carbon. This is made the cathode. The anode consists of 3 or 4 stout carbon rods attached to a rod of copper and is suspended in the molten bath. A little fluorspar is added to increase the fluidity of the bath. When electric current is passed in, alumina undergoes decomposition. Aluminium, liberated at the cathode, sinks in the liquid state to the bottom whence it is taken out by means of the tap-hole. Oxygen, liberated at the anode, attacks the carbon rod producing CO and CO_2 which are given off as gas.

$$2Al_2O_3 = 4Al + 3O_2.$$

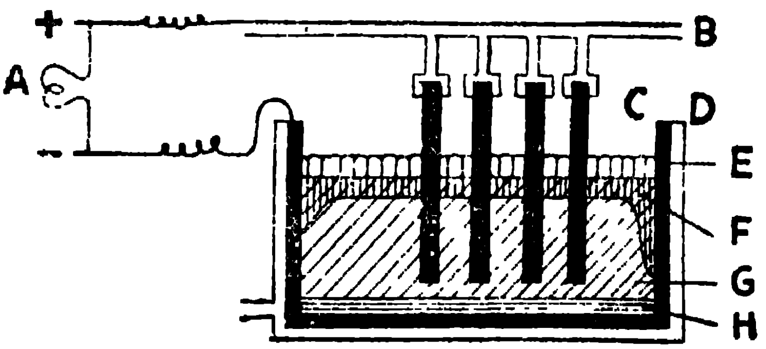


Fig. 34

The resistance of the electrolyte gives sufficient heat to keep the mass in the fused condition. The temperature of the bath is usually maintained at about 900°C.

The method is continuous. When Al_2O_3 is used up, the resistance of the furnace increases and then a lamp which is shunted off the circuit, begins to glow. Fresh Al_2O_3 is then added.

(*a*) Dilute nitric acid very slowly attacks impure aluminium giving aluminium nitrate and ammonium nitrate, but pure aluminium is not acted upon by nitric acid, particularly when the acid is concentrated.

(*b*) When hydrogen chloride is passed over the heated metal, anhydrous aluminium chloride is formed which readily sublimes off and collects in a cooled receiver used in the reaction. Hydrogen gas is also evolved which escapes,

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

(*c*) Aluminium chloride solution, due to hydrolytic decomposition, always contains a little HCl. So when aluminium is dipped into such a solution, a few bubbles of hydrogen are evolved and HCl is thereby destroyed. The solution then undergoes progressive hydrolysis and aluminium hydroxide, $Al(OH)_3$, will be deposited to a certain extent as a gelatinous precipitate. But these reactions will be very feeble.

Q. 4. *Enumerate the changes that take place when* (*a*) *carbon dioxide is passed into lime water,* (*b*) *sulphuretted hydrogen is passed through a concentrated solution of sulphur dioxide in the cold,* (*c*) *chlorine is passed into hot milk of lime,* (*d*) *nitric oxide is led into a solution of ferrous sulphate which is subsequently heated.*

Express the chemical reactions by equations and also name the products as far as possible.

Ans. (*a*) When carbon dioxide is passed into lime water in moderate amount, a white precipitate of calcium carbonate is formed, rendering the solution milky.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

On passing more CO_2, so that it is in excess, the milkiness of the solution disappears due to the precipitated $CaCO_3$ passing into solution as calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

(*b*) When sulphuretted hydrogen is slowly passed through a concentrated solution of sulphur dioxide in the cold, a milky solution, containing precipitated colloidal sulphur, known as *Wackenroder's solution*, is obtained. Though sulphur is the main product obtained as a precipitate, the solution contains thionic acids and chiefly pentathionic acid, $H_2S_5O_6$,

The primary chemical reaction is represented by the equation, $2H_2S + SO_2 = 2H_2O + 3S$ and the pentathionic acid formation is represented by the equation, $5H_2S + 10SO_2 = 3H_2S_5O_6 + 2H_2O$.

(*c*) When chlorine is passed into hot milk of lime, calcium chlorate and calcium chloride are formed along with water.

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

(*d*) When nitric oxide is passed into a solution of ferrous sulphate, it is absorbed by ferrous sulphate solution giving a brown solution which contains a loose compound of ferrous sulphate and nitric oxide of the composition $FeSO_4$, NO.

$$FeSO_4 + NO = FeSO_4, NO.$$

When the brown solution containing $FeSO_4$, NO is heated, nitric oxide escapes and ferrous sulphate remains behind in solution.

$$FeSO_4, NO = FeSO_4 + NO.$$

Q. 5. *Briefly describe the metallurgy of iron. What ingredients are used in India for its preparation ?*

How are these obtained : (a) malleable iron from pig iron, (b) passive iron, and (c) rustless iron ?

Ans. The ores generally employed for the extraction of iron are the oxides and the carbonate. These ores are first roasted in order to drive off water and carbon dioxide. to render the mass porous and to convert the ferrous oxide to ferric oxide. The oxide, thus obtained, is then reduced with coke and limestone in a blast furnace. The blast furnace is made of steel and lined inside with fire-bricks. It is from 50 to 80 ft. in height and is broadest at the middle. The top of the furnace is closed by a *cup-and-cone* arrangement. The calcined ore mixed with coke and limestone, is introduced into the furnace, by lowering the cone. A blast of heated air at a temp. of 700°—800°C. is then introduced through the jets at the bottom, known as tuyeres, placed round the base of the furnace. The oxygen of the air combines with the carbon to form carbon monoxide which brings about the reduction of the iron oxide to iron.

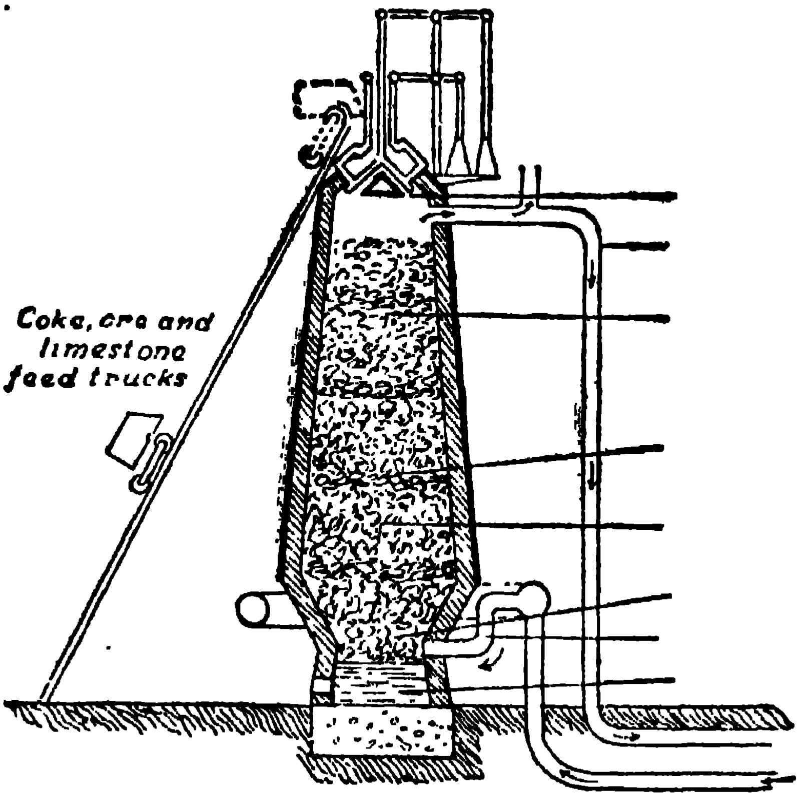


Fig. 35

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

A portion of Fe_2O_3 that may escape reduction by CO is reduced by carbon itself. The spongy iron so obtained at a temp. of 1000°C., absorbs various impurities like carbon, sulphur, phosphorus and silicon from the ore, coke, etc. This impure iron melts and descends to the bottom of the furnace. Lime obtained by the decomposition of the limestone at the temperature of the furnace, combines with the siliceous impurities present in the ore forming a slag which flows down with the molten iron to the hearth. The slag, being lighter than the molten iron, floats on its surface, and thus prevents oxidation of the iron by the oxidising action of the blast.

$$CaCO_3 = CaO + CO_2$$
$$CaO + SiO_2 = CaSiO_3 \text{ (Slag)}$$

As the slag reaches a certain height, it runs out through certain openings known as slag-holes : the iron is run off at suitable intervals and allowed to flow into moulds of sand. Iron, thus obtained, is known as pig iron or cast iron.

In India, Red haematite and Brown haematite are obtainable in different localities like Mayurbhunj, Keonjhur, Mysore, etc., and these are used in the extraction of iron. Coal obtainable in abundance, is converted into coke in coke-ovens and used in the blast furnace along with the fluxes like dolomite ($MgCO_3$, $CaCO_3$) and limestone, $CaCO_3$.

(*a*) *Preparation of wrought iron from pig iron*—Wrought iron is obtained from cast iron by oxidising away the impurities of molten cast iron by contact with ferric oxide in a *puddling furnace*. The *puddling furnace* is essentially a reverberatory furnace, the side-plates and bottom of the hearth being lined with *fettling* (ferric oxide). Cast iron is melted in the hearth of the furnace and is then well stirred with long iron rods to mix the molten mass with the lining, and also to expose every part of the molten metal to the oxidising action of air. Silicon and manganese are first oxidised and then the carbon is attacked as also sulphur. Volatile gases like CO_2, SO_2 escape and the non-volatile oxides combine with the iron oxide of the lining, producing slag. Due to escape of gases, the metal seems to boil. As the iron becomes purer, its melting point rises ; but the temperature of the furnace not being high enough, the mass becomes pasty. The pasty mass is then worked into balls and hammered under steam hammers to squeeze out the slag. The product, which is rolled into sheets or bars, and cooled, is wrought iron containing a very low amount of impurity.

(*b*) Passive iron is obtained by dipping iron in fuming nitric acid, or chloric acid, or chromic acid or even in hydrogen peroxide. Iron then becomes insoluble in dilute acids and loses its capacity to deposit copper when dipped into a solution of copper sulphate.

(*c*) An alloy known as chromium steel is known as rustless iron, or stainless steel. It is produced by adding ferro-chrome, *i.e.*, iron with 60-70 per cent. of chromium, to steel produced by the open-hearth process, before the molten steel is poured out on the laddle. Stainless steel contains 12-14 per cent. of chromium as ordinarily prepared. Rustless iron can also be obtained by giving iron a coating of Fe_3O_4 by passing steam over iron rendered red-hot. Under the circumstances rusting of iron is prevented.

Q. 6. *How does calcium occur in nature? What are the chief compounds of calcium that are extensively used for various purposes? Give a brief review of the methods that lead to the industrial production of these materials.*

Ans. Calcium occurs in nature as

(1) Carbonate, $CaCO_3$, in calcite, aragonite, limestone, calcspar, chalk, etc.;

(2) double carbonate with magnesium;
$MgCO_3$, $CaCO_3$, in dolomite;

(3) sulphate, $CaSO_4$, $2H_2O$, in gypsum;

(4) phosphate, $Ca_3(PO_4)_2$, in phosphorite;

(5) fluophosphate, $3Ca_3(PO_4)_2$, CaF_2 in fluorapatite; chloro-phosphate, $3Ca_3(PO_4)_2$, $CaCl_2$, in chlorapatite;

(6) fluoride, CaF_2, in fluorspar.

The chief compounds of calcium that are extensively used in industry and for various other purposes are (*a*) lime, both quicklime, CaO and slaked lime, $Ca(OH)_2$; (*b*) bleaching powder, Ca(OCl)Cl; (*c*) plaster of Paris, $2CaSO_4$, H_2O and (*d*) calcium carbide, CaC_2.

(*a*) Both quicklime and slaked lime are obtained from lime stone, $CaCO_3$. Lime kiln, a shaft furnace in construction, is filled with blocks of limestone. The lumps of limestone are arranged in the form of an arch over the fire obtained by burning carbon-aceous fuel below. The arrangement is such that the fuel is kept separate from the stone (see Fig. 36). The burning is carried on for thirty-six to forty-eight hours. The kiln is then allowed to cool and the lumps of quicklime are then taken out. This process is non-continuous and is wasteful of fuels and so at present continuous lime-kilns are in operation. Producer gas is used as a fuel in this case and lime gradually comes down the kiln and is taken out at the bottom, more limestone being fed at the top.

$$CaCO_3 = CaO + CO_2.$$

When quicklime is treated with water in small amount, much heat is developed and steam is produced. The quicklime

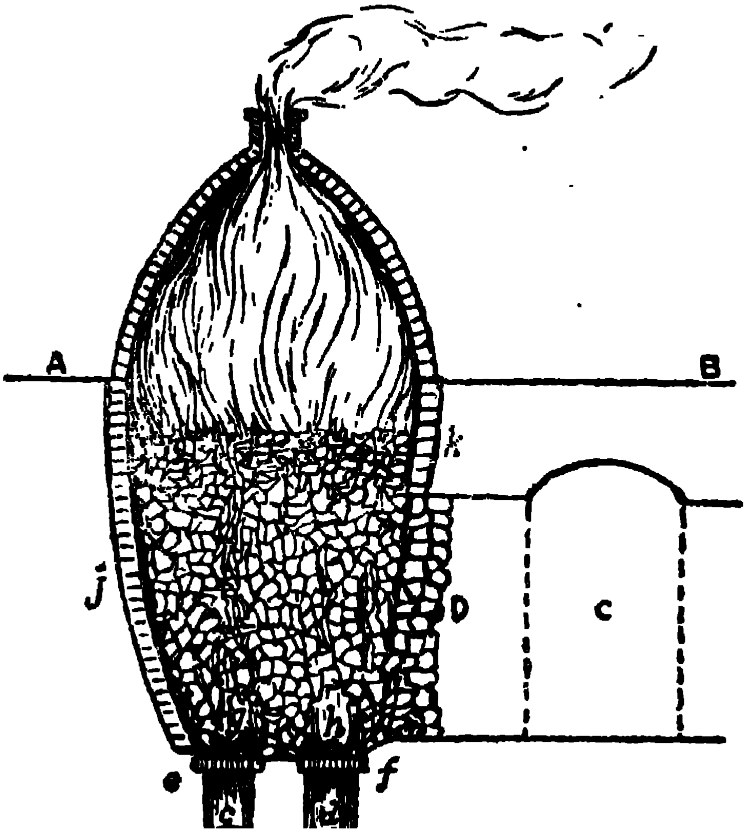


Fig. 36

cracks and finally, when sufficient water has been added, it crumbles down to a fine white powder. This is calcium hydroxide, produced by combination of water with quicklime, $CaO + H_2O = Ca(OH)_2$. Thus slaked lime, $Ca(OH)_2$, is obtained.

(*b*) Dry slaked lime, $Ca(OH)_2$, is spread on the floor of a lead-lined wooden chamber, provided with glass doors and windows and a fan arrangement inside the chamber for dusting in lime. Chlorine, free from CO_2 and HCl, is led in by a pipe near the top. The temperature is not allowed to rise above 40°C., and the mass is left in that condition for about 24 hours. In the meantime lime is turned over with wooden rakes from time to time inorder to expose fresh surface to the action of chlorine gas. When the absorption of chlorine is nearly complete, some lime is sprayed into the chamber with the help of the fan arrangement inorder to get rid of the last trace of chlorine. Bleaching powder is then removed by workmen by removing the false bottom of the chamber and packed into barrels.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

(c) Plaster of Paris, $2CaSO_4, H_2O$, is prepared by heating gypsum to a temperature not exceeding 120°C. in a furance in such a fashion that it does not come in contact with carbonaceous fuel to avoid reduction.

$$2CaSO_4, 2H_2O = (CaSO_4)_2, H_2O + 3H_2O.$$

(*d*) Calcium carbide is prepared by heating a mixture of 2 parts of coke and 3 parts of quicklime to a high temperature in a closed electric furnace. The carbide is produced in the fused state at the high temperature of the furnace and is tapped off, cooled and broken up into pieces.

$$CaO + 3C = CaC_2 + CO.$$

Q. 7. *What is glass ? How is it prepared ? What do you know about making glass vessels ?*

Give a short account of the following :—

(a) Transparent silica, (b) flint glass, and (c) ruby glass.

Ans. Glass is an amorphous, transparent or translucent substance which can be considered as a super-cooled liquid. It is rigid in structure and is of infinite viscosity. It is not a single individual chemical unit, but is an intimate mixture of several substances, all silicates, one of which must always be that of an alkali metal. The usual silicates are those of sodium, potassium, calcium or lead. The silicates are formed at a high temperature at which they are all in the fused state. In that fused condition they mix and when this molten mixture cools down the individual silicates do not separate but remain mixed together. The liquid mixture of silicates, as it cools down, passes through a plastic condition to the very hard, brittle and transparent substance known as glass, which has no crystalline structure or sharp melting point. When heated, glass becomes gradually softer and softer as the temperature rises, and is ultimately transformed into a mobile liquid. On cooling, glass passes through all degrees of viscosity which makes the manufacture of glass articles by blowing possible and its manipulation easy. It is a non-conductor of heat and electricity. Ordinary glass vessels undergo unequal expansion in different directions on sudden heating. So the sudden heating of glass vessels invariably cause the cracking and destruction of the vessel. Glass is generally resistant to the action of most chemicals but is slowly attacked by water even at the ordinary temperature. It is acted on by alkalies and by hydrofluoric acid forming silicon tetra-fluoride. Glass, may be highly polished and beautifully coloured and hence its extensive use in arts. Glass develops the tendency of losing its transparency and becoming porcelain-like white in appearance spontaneously sometimes at the ordinary temperature and always when kept continuously at high temperature. This is due to the crystallisation of the component silicates. This is known as *devitrification.* Pieces of glass may be welded together by fusion, a property which is found to be of much value.

Composition and classification of glass :—

The chemical composition of glass is not that of one single compound ; so it is difficult to give any particular chemical formula to it. Yet, within certain limits, it may be approximately represented by the formula xA_2O, yBO, $6SiO_2$, where "A" stands for either sodium or potassium and "B" stands for either calcium or lead and usually x and y are found to be equal to 1.

Commercial glass, as is usully met with, may be classified into the following *four* chief classes :—

I. Soda-lime glass, soft glass or crown glass.—Na_2O, CaO, $6SiO_2$.—It is mainly a mixture of sodium and calcium silicates. It is very fusible. Window glass, plate glass and the glass of majority of laboratory apparatus belong to this class.

II. Potash-lime glass, Bohemian glass or Hard glass.—K_2O, CaO, $6SiO_2$.—It is chiefly a mixture of potassium and calcium silicates. It fuses at high temperatures and with great difficulty. It is very resistant to the action of solvents. These properties make it suitable for the construction of chemical apparatus and combustion tubes.

III. Potash-lead glass or flint glass.—K_2O, PbO, $6SiO_2$.—This is mainly a mixture of potassium and lead silicates. It fuses very readily and hence can be worked with easily. This variety of glass is characterised by possessing a brilliant lustre due to its high refractive index and is, therefore, largely used in the manufacture of lenses, prisms and other optical apparatus. The presence of lead in this variety makes it incapable of being heated in reducing flames which will reduce the lead present to the metallic state and render the glass black and opaque. It is readily attacked by aqueous solutions.

IV. Bottle glass or common glass.—This is a mixture of sodium, calcium and iron silicates. It is yellow, brown or green in colour. It is less fusible than soda-lime glass. It is more readily attacked by acids. It is used for the manufacture of ordinary bottles and medicine phials.

Manufacture of glass :—

The materials required for the manufacture of glass are chiefly the alkalies, lime and silica. The alkalies are supplied in the form of carbonates and sulphates of sodium and potassium. Lime is supplied in the form of chalk or limestone. Lead is used in the form of red lead, litharge or white lead. Silica is supplied in the form of clean white sand or quartz.

The materials used should be thoroughly free from iron and carbonaceous matter, for these materials impart objectionable colour to glass. If the materials cannot be had free from iron and carbon, they are oxidised towards the end by addition of pyrolusite or nitre in case of lime glass or red lead in case of lead glass.

The materials are first mixed with broken glass called *cullet*. These are then finely powdered in grinding machines and are very accurately weighed in right proportions and then intimately mixed. The mixing is done in mixing machines so as to make the mixture as uniform as possible. The mixture (technically called the *batch*) is then put into specially constructed pots of refractory fireclay (open or covered) or in tanks also made of fireclay, in small quantities at a time and heated to a high temperature by means of producer gas. When the first charge has melted, a second is added and the charge melted. The process is continued until the pots are nearly full. At this stage, substances required for oxidation and decolorisation, *viz*., pyrolusite, nitre, red lead, etc., are added and the mixture heated for some time until CO_2, SO_2, and O_2 are all evolved away. The whole charge melts to quiet fusion at this stage. The temperature is then still further raised and the melt left for sometime in that condition. The scum that is formed is removed. When the molten mass is free from bubbles and glass galls, the temperature of the molten liquid is allowed to fall slowly, so that the glass becomes plastic enough to work with.

If coloured glass is to be produced by the *pot-metal colouring* process, colouring materials, usually suitable metallic oxides, are added to the molten glass and the mass heated again till it becomes homogeneous. Thus, FeO produces green glass, CoO blue glass, Cu_2O red glass, etc.

Glass vessels are made either by blowing glass in the plastic condition, or by pouring molten glass in moulds. The vessels produced in the second way are progressively cooled by passing them through several chambers the temperature of which gradually comes down. These are called annealing chambers and the process is called annealing.

(*a*) Transparent silica, or silica glass is obtained by fusing any form of silica in the electric furnace. Its co-efficient of cubical expansion is very small and so a vessel made of fused silica can be made red-hot and dipped into water without cracking. It is transparent to ultraviolet light.

(*b*) Flint glass is, as stated before, potash-lead glass. It is mainly a mixture of potassium and lead silicates, the composition of which can be approximately represented by the formula, $K_2O, PbO, 6SiO_2$. It is prepared in hooded pots, otherwise it turns black due to separation of lead. It is of higher specific gravity than ordinary glass and has a bright lustre. The refractive index (1·70 – 1·78) is also higher than that of any other kinds of glass. It is acted upon by aqueous solutions readily.

(*c*) Ruby glass is a kind of glass coloured red by the addition of either cuprous oxide, or purple of Cassius to the fused glass during its manufacture. It is used in the manufacture of fancy articles, window panes and in the production of artificial gems.

Q. 8. *How can you convert (a) ferric chloride into ferrous chloride, (b) stannous chloride into stannic chloride, (c) mercurous nitrate into mercuric nitrate and (d) cupric chloride into cuprous chloride.*

Express the changes by equations and justify the statement that these reactions involve an oxidising or a reducing process.

Ans. (*a*) On passing sulphur dioxide through a yellow solution of ferric chloride, a colourless or (faintly green) solution of ferrous chloride is produced.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

Here the proportion of the electro-negative element, chlorine in ferric chloride, is diminished and so it is a case involving reduction.

(*b*) Stannous chloride is taken in a hard glass tube and heated, and chlorine gas from a chlorine cylinder is passed over it, when chlorine combines with stannous chloride giving stannic chloride.

$$SnCl_2 + Cl_2 = SnCl_4.$$

Here the proportion of the electro-negative element, chlorine in stannous chloride, is increased and so it is a case involving oxidation.

(*c*) Mercurous nitrate is taken in a test tube and boiled with conc. HNO_3, when mercuric nitrate is formed.

$$Hg_2(NO_3)_2 + 4HNO_3 = 2Hg(NO_3)_2 + 2H_2O + 2NO_2.$$

Here the proportion of the electro-negative radical, NO_3, in mercurous nitrate, is increased and so it is a case involving oxidation.

(*d*) A solution of cupric chloride is taken in a test tube and sulphur dioxide gas is passed through it, when white ppt. of cuprous chloride is obtained.

$$2CuCl_2 + 2H_2O + SO_2 = Cu_2Cl_2 + H_2SO_4 + 2HCl.$$

Here the proportion of the electro-negative element, chlorine in cupric chloride, is diminished and so it is a case involving reduction.

FIRST PAPER—1946

Q. 1. *Explain and illustrate the following :—*

(a) Atoms and molecules ; (b) oxidation and reduction. What do you understand by the statement—"The atomic weight of chlorine is 35·5" ?

Ans. (*a*) **Atoms :** An atom of an element is the smallest particle of that element which can take part in a chemical change. According to **Dalton's atomic theory** an atom is incapable of separate existence. But in case of monatomic elements like inert gases of argon family, atoms of those elements exist in the free state.

Molecules : A molecule of any substance, either elementary or compound, is the smallest particle of that substance which can exist in the free state preserving all charateristics of that substance. Molecules are made up of one or more atoms of the same element (in the case of elementary substances) or two or more atoms of different elements (in the case of compounds).

Thus a molecule of mercury or sodium in the vapourous state consists of only one atom of the partientar element ; the molecule of hydrogen, oxygen or nitrogen (elementary gaseous substances) consist of 2 atoms each of the element concerned ; a molecule of hydrochloric acid and of steam (compound vapourous substances) consists of 2 atoms and 3 atoms respectively of different elements. A molecule of calcium carbonate consists of 5 atoms, 1 of calcium, 1 of carbon and 3 of oxygen.

(*b*) **Oxidation** is described as the process which increases the proportion of oxygen or of an equivalent electro-negative element or radical in an element or a compound, or diminishes the proportion of hydrogen or of an electro-positive element or radical in a compound.

Reduction may be defined as the result of the converse operations. Thus, **reduction** is the process which increases the proportion of hydrogen or of an electro-positive element or radical in an element or a compound, or diminishes the proportion of oxygen or of an equivalent electro-negative element or radical in a compound.

Thus, when sulphur is burnt in oxygen, it is **oxidised** to sulphur dioxide.

$$S + O_2 = SO_2.$$

When iron is heated in a stream of chlorine gas, it is oxidised to ferric chloride.

$$2Fe + 3Cl_2 = Fe_2Cl_6.$$

When hydrochloric acid is heated with manganese dioxide, it is oxidised to chlorine by removal of hydrogen.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

Similarly, when hydrogen gas is passed over heated copper oxide (black), it is reduced to metallic copper (red).

$$CuO + H_2 = Cu + H_2O.$$

When sulphuretted hydrogen is passed into iodine suspended in water, iodine is reduced to hydriodic acid by addition of hydrogen.

$$H_2S + I_2 = 2HI + S.$$

When ferric chloride solution (yellow) is treated with zinc and hydrochloric acid, it is reduced to ferrous chloride (solution colourless) by nascent hydrogen.

$$FeCl_3 + H = FeCl_2 + HCl.$$

Among inorganic compounds, oxidation usually denotes an increase in the active valency of the central atom, as for example, when ferrous chloride is oxidised to ferric chloride, or stannous chloride is oxidised to stannic chloride.

From ionic standpoint, if we take into consideration the reaction,

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2,$$

it can be represented as

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised by the loss of two electrons which have passed to the two ferric ions, reducing them to the ferrous state.

Hence, *oxidation* may be defined as *a loss of electrons* and *reduction* as *a gain of electrons.*

Moreover, it must also be observed that oxidation and reduction take place simultaneously. Whenever a substance is oxidised, another one is reduced. Thus, when stannous chloride solution is added to a solution of mercuric chloride, a white precipitate of mercurous chloride is obtained. Here mercuric chloride is reduced to mercurous chloride, but at the same time stannous chloride is oxidised to stannic chloride.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

By the statement—"*The atomic weight of chlorine is 35·5*", we mean to say that the weight of one atom of chlorine is 35·5 times the weight of one atom of hydrogen.

$$\text{Thus, } \frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of hydrogen}} = 35{\cdot}5.$$

But at present the hydrogen standard of the atomic weights of elements has to be given up and oxygen with the value 16·00 has been accepted as the standard of atomic weights. On that basis the statement means

$$\frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of oxygen}} \times 16 = 35{\cdot}5.$$

Q. 2. *Both nitrous oxide and air contain nitrogen and oxygen. How would you prove that in one they are chemically combined while in the other they form a mechanical mixture ?*

Describe how you would determine the composition of air as well as of nitrous oxide by volume and then deduce the molecular formula of the latter.

Ans. Air is a mechanical mixture of nitrogen and oxygen, whereas nitrous oxide is a chemical compound of nitrogen and oxygen.

The following are the reasons for considering air to be a mechanical mixture of nitrogen and oxygen :—

(1) In a mechanical mixture of two or more substances the properties of the different ingredients are retained, but when a compound is formed from two or more ingredients, the molecules of the ingredients are changed and new molecules are formed. These new molecules have properties altogether different from those of the ingredients.

Thus, the properties of both nitrogen and oxygen are found to be present in air ; for example, oxygen is a supporter of combustion, so is also air, though to a less extent on account of its dilution. Oxygen is absorbed by alkaline pyrogallate, while oxygen present in air is also absorbed by alkaline pyrogallate. But alkaline pyrogallate cannot remove oxygen by absorption from any of the oxides of nitrogen which are compounds of nitrogen and oxygen. After removal of oxygen from air by absorption with alkaline pyrogallate, nitrogen left shows all the properties of nitrogen.

Therefore air is considered to be a mechanical mixture.

(2) The analyses of samples of air drawn from different localities and different altitudes show that the proportion of nitrogen and oxygen in air by weight is *nearly* constant, yet slight variations are noticeable. But even the slightest deviation is not possible in the case of a chemical compound.

Air is thus a mixture of oxygen and nitrogen.

(3) When gases combine chemically, there is always a thermal effect, and oftentimes a change in volume is observed. But when 23 parts by weight of oxygen are mixed with 77 parts by weight of nitrogen, there is neither any heat change nor any change in volume. Yet the mixture behaves in every way like ordinary air.

Thus, air is a mechanical mixture.

(4) The density and other physical properties of air are average of these properties of the constituents, nitrogen and oxygen, in the proportion in which they are present in air. Thus, taking d to be the density of air which contains nitrogen and oxygen in the proportion 4 : 1 by volume approximately, we can calculate d as follows :—

Wt. of air = Wt. of nitrogen + wt. of oxygen. Taking into consideration 100 vols. of air to be formed from 80 volumes of nitrogen and 20 vols. of oxygen,

$$\begin{aligned} 100 \times d &= 80 \times 14 + 20 \times 16 \\ &= 1120 + 320 \\ &= 1440 \\ \therefore\ d &= 14{\cdot}4 \end{aligned}$$

The observed density of air is also 14·4—just the value calculated on the assumption that air is a mechanical mixture.

Therefore air is nothing but a mechanical mixture.

(5) There are five different oxides of nitrogen whose gravimetric compositions are such that they obey the *Law of Multiple proportions*. The composition of air by weight (77 nitrogen : 23 oxygen) is such that no simple formula can be assigned to it. (77 parts by weights of nitrogen stand for 5½ atoms of nitrogen and 23 parts by weight of oxygen stand for 1·4375 atoms of oxygen). Thus the Law of Multiple proportions as applied to the case of definite oxides of nitrogen cannot be applied here.

Therefore air is a mechanical mixture.

(6) The ingredients of a mechanical mixture can be separated by easy mechanical means of separation like diffusion, distillation, vaporisation, etc., but the components of a chemical compound cannot be so separated.

The constituents of air can be separated

(*a*) *By diffusion* : When air is passed through a porous tube, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen and the residue left is found to be richer in oxygen than ordinary air. Had air been a chemical compound, no such separation of the constituents would have been possible.

(*b*) *By vaporisation* : When liquid air is allowed to evaporate, the boiling point increases progressively. Furthur, the gas which comes out first is richer in nitrogen than the gas which comes out afterwards. Thus, liquid air is to be considered as a mixture of two liquids, liquid nitrogen and liquid oxygen, and it may be presumed that atmospheric air is also a mixture of the gases, nitrogen and oxygen.

(*c*) *By solution in water :* If air be shaken with water, a part of it goes into solution and the dissolved gas can be expelled by boiling. It has been found that the air thus recovered from solution is very much richer in oxygen than ordinary air. Thus a partial separation of the ingredients of air by solution in water followed by subsequent heating, *i.e.*, by easy mechanical means, is possible.

Air is thus a mechanical mixture.

Any single argument given in the above discussion may not be considered sufficient, but the arguments taken all together prove completely that air is a mechanical mixture, and *not a compound*, of nitrogen and oxygen.

But nitrous oxide does not satisfy any of the tests applied in the case of air and the characteristics of definite compound of nitrogen and oxygen are present here. Thus,

(1) Oxygen in nitrous oxide cannot be removed by absorption with alkaline pyrogallate, nor the oxygen in it produces brown fumes with nitric oxide (a characteristic of free oxygen).

(2) Oxygen present in nitrous oxide cannot be separated by easy mechanical means as mentioned in the case of separation of oxygen from air.

(3) Whatever may be the source of nitrous oxide, it has always the same composition by weight, *viz.*, 7 parts by weight of nitrogen combined with 4 parts by weight of oxygen.

(4) In the formation of nitrous oxide from nitrogen and oxygen, heat is absorbed and heat is given up during its decomposition.

(5) The volumetric composition of the gas nitrous oxide can be utilised for determining its formula and its density agrees with the formula so derived.

(6) In nitrous oxide 2 volumes of nitrogen combining with 1 volume of oxygen give rise to 2 volumes of nitrous oxide but in air 4 volumes of nitrogen and 1 volume of oxygen give rise to exactly 5 volumes of air.

Composition of air by volume :

A long glass tube, closed at one end, is taken and it is divided into six equal divisions by five rubber rings. Next a freshly prepared solution of pyrogallic acid in excess of caustic soda solution is poured into the tube so as to fill up exactly one division. The open end of the tube is then closed with the thumb and the tube thoroughly shaken so that the whole of oxygen is absorbed by the alkaline pyrogallate solution. Then the tube still closed with the thumb is inverted over water contained in a tall jar. The thumb is then removed and the water is found to rise up the tube. The level of water inside and outside the tube is then adjusted to the same height. The surface of water is found to stand at the second ring from the open end of the tube. Thus we find that out of 5 vols. of air taken, 1 vol. must have been occupied by oxygen, which is absorbed by alkaline pyrogallate, and water rises up to fill this 1 vol., while the remaining 4 vols. are occupied by nitrogen. That the remaining gas is nitrogen is proved by the facts that (*a*) it is inert, (*b*) it does not support combustion and (*c*) it is absorbed by heated magnesium.

Thus air is a mixture of nitrogen and oxygen in the approximate proportion of 4 : 1 by volume.

Composition of nitrous oxide by volume and deduction of its molecular formula :—

The volumetric composition of nitrous oxide is determined by the *thumb tube method.*

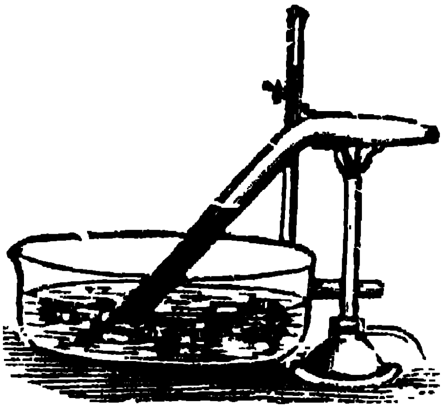


Fig. 37

Nearly half of a thumb tube is filled up with dry nitrous oxide by the displacement of mercury, the thumb tube with its contents being placed in a deep jar of mercury as shown in the adjoining figure.

Into the horizontal portion of the tube a small piece of sodium is introduced. The level of mercury inside and outside the tube is made the same and the volume of nitrous oxide noted. Next, the piece of sodium is heated from outside when it catches fire and combines with all the oxygen of nitrous oxide.

giving oxides of sodium which are solid. Nitrogen gas is left behind as determined by suitable tests. The apparatus is allowed to cool and the level of mercury is adjusted. The mercury level stands exactly at the same place as before. That the gas left is nitrogen is proved by the facts that it is inert, does not turn lime-water milky and is completely absorbed by strongly heated magnesium. Thus, it is proved that nitrous oxide contains its own volume of nitrogen.

Deduction of molecular formula of nitrous oxide :—

From the above experiment we know that one vol. of nitrous oxide contains 1 vol. of N_2. Let "n" be the number of molecules present in 1 vol. of nitrous oxide. Then n molecules of nitrous oxide contain n molecules of N_2. Therefore, 1 molecule of nitrous oxide contains 1 molecule of nitrogen, that is, 2 atoms of nitrogen, since nitrogen molecule is diatomic (Deduction from Avogadro's hypothesis). Thus, the formula for nitrous oxide is N_2O_x, where x is an integer. Now, the density of nitrous oxide, as determined experimentally, is 22. Therefore, the molecular weight of nitrous oxide is 44. Of these 44 parts, 28 is accounted for by nitrogen, and 16 parts to be accounted for by oxygen. But 16 is the atomic weight of oxygen. Therefore, $x=1$ and the molecular formula for nitrous oxide is N_2O.

Q. 3. *How is acetylene prepared in the laboratory? State its properties and uses.*

Calculate the percentage of potassium chlorate in a commercial sample of the material, contaminated with potassium chloride, 1·555 grams of which liberate, when fully decomposed, just sufficient oxygen for the complete combustion of 152 c.c. of acetylene gas at 27°C. and 750 mm. pressure.

Ans. Preparation of acetylene in the laboratory is carried out in an Erlenmeyer flask fitted with a dropping funnel and a delivery tube. Small lumps of calcium carbide are placed on a layer of sand taken inside the dry Erlenmeyer flask at the mouth of which a cork is fitted carrying the dropping funnel and the delivery tube. Water is gradually dropped upon the lumps of calcium carbide from the dropping funnel, when acetylene gas is freely evolved. The gas is collected by displacement of water.

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$$

Acetylene is a colourless gas, which in the pure state has an ethereal smell. Usually due to presence of impurities the gas possesses a garlic odour. It is slightly lighter than air. It is more soluble in water than methane or ethylene. It readily dissolves in alcohol. The gas is combustible, and is a nonsupporter of combustion. It burns with a highly luminous smoky flame, the smoke being due to separation of free carbon from acetylene by decomposition at an elevated temperature. When mixed with air and oxygen, the gas explodes on firing.

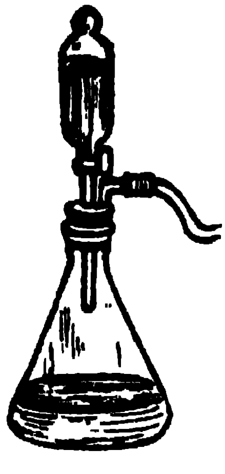


Fig. 38

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

When the gas is passed into ammoniacal solution of cuprous chloride, a red precipitate of copper acetylide, Cu_2C_2, H_2O is formed. When passed into ammoniacal silver nitrate solution, acetylene gives a white precipitate of silver acetylide. When mixed with hydrogen and passed over spongy platinum, ethylene and ultimately ethane is formed.

$$C_2H_2 + H_2 = C_2H_4, \; C_2H_4 + H_2 = C_2H_6.$$

It is absorbed by bromine water, forming acetylene bromides and when brought into contact with chlorine it bursts into flame.

$$C_2H_2 + Cl_2 = 2C + 2HCl.$$

When the gas is passed into a solution of mercuric sulphate in H_2SO_4 at 50° – 60°, it combines with water giving acetaldehyde.

$$C_2H_2 + H_2O = CH_3CHO.$$

Acetylene is used for illuminating purposes where coal gas is not available ; for generating oxy-acetylene flame required for welding pieces of iron and steel together and it is admixed with coal gas, oil gas, etc. to increase their luminosity.

Let V c.c. be the volume of acetylene at N.T.P. Then by Boyle's and Charles' Laws, we have,

$$\frac{152 \times 750}{273 + 27} = \frac{V \times 760}{273}$$

$$\therefore \quad V = \frac{152 \times 750 \times 273}{300 \times 760} \text{ c. c.}$$

$$= \frac{38 \times 273}{76} \text{ c. c.} = \frac{273}{2} \text{ c. c.} = 136{\cdot}5 \text{ c.c.}$$

Now, from the equation,

$$\begin{array}{ll} 2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O \\ \text{2 vols.} \quad \text{5 vols.} \end{array}$$

2 vols. of acetylene require 5 vols. of oxygen for complete combustion under the same conditions of temp. and pressure.

$\therefore$ 136·5 c. c. of acetylene at N.T.P. will require for complete combustion $136{\cdot}5 \times \frac{5}{2}$ c. c. or $\frac{682{\cdot}5}{2}$ c. c. or 341·25 c. c. of oxygen at N.T.P.

From the equation,

$$\begin{array}{ll} & 2KClO_3 = 2KCl + 3O_2 \\ 2 \times (39 + 35{\cdot}5 + 48) & \qquad 3 \times 32 \end{array}$$

We know that $2 \times 122{\cdot}5$ gms. of $KClO_3$ will give rise to 3×32 gms. of O_2. But molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P. Therefore, $3 \times 22{\cdot}4$ litres of oxygen at N.T.P. can be obtained from $2 \times 122{\cdot}5$ grams of $KClO_3$. Hence 341·25 c. c. or 0·34125 litres of oxygen at N.T.P. will be obtained from $\frac{2 \times 122{\cdot}5}{3 \times 22{\cdot}4} \times 0{\cdot}34125$ grams or 1·245 grams of $KClO_3$. Hence in 1·555 grams of impure potassium chlorate, there are present 1·245 grams of $KClO_3$, the rest being the impurity, potassium chloride.

Hence, the percentage of $KClO_3$ present in the commercial sample of potassium chlorate

$$= \frac{1{\cdot}245 \times 100}{1{\cdot}555} = 80{\cdot}04.$$

Q. 4. *Describe the isolation of fluorine and give a neat sketch of the apparatus used. Compare its properties with those of chlorine.*

Ans. Fluorine was isolated by Moissan by electrolysing a solution of potassium hydrogen fluoride, KF, HF (Fremy's salt) in anhydrous hydrofluoric acid, HF. Anhydrous HF is a non-conductor of electricity, but it is rendered conducting by dissolving KF, HF in it. The apparatus for electrolysis consists of a U-tube made of an alloy of Platinum and Iridium provided with two side-tubes and is fitted with fluorspar stoppers. Two electrodes made also of Platinum-Iridium alloy and thickened at the bottom pass through the fluorspar stoppers. The whole apparatus is kept immersed in a bath of boiling methyl chloride at −23°C. The U-tube is $\frac{2}{3}$rd filled up with the electrolyte which is a solution of potassium hydrogen fluoride in anhydrous hydrofluoric acid. On passing the current through the electrolyte, Hydrogen is liberated at the cathode and Fluorine at the anode. The gas evolved at the anode is next passed through a spiral of Platinum tube kept immersed in boiling methyl chloride to remove any vapour of HF coming over by condensation. The last trace of HF vapour is removed by passing the gas through a tube of Platinum packed with sodium fluoride, NaF. Hydrogen liberated at the cathode was collected and measured by Moissan, who also absorbed the gas from the anode in iron wire in a weighed platinum tube. He found that for every gram of hydrogen evolved at the cathode the increase in weight of the Platinum tube containing iron wire was 19 grams. The gas evolved at the anode was thus established to be Fluorine.

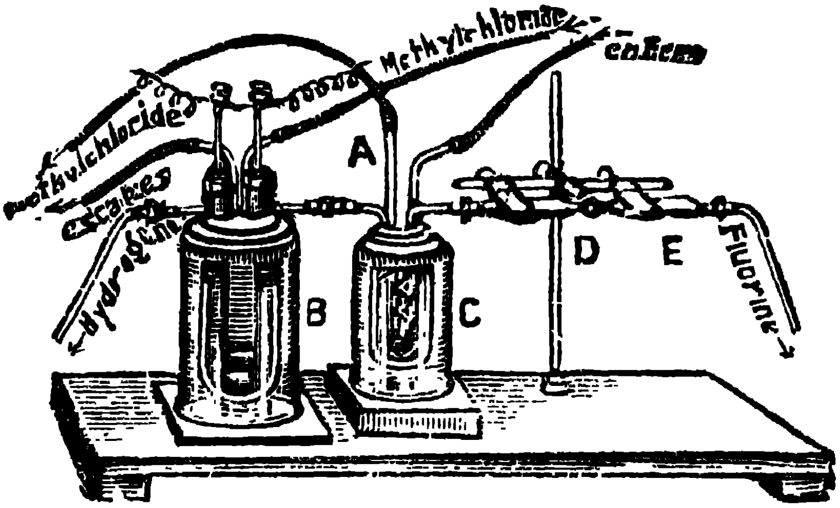


Fig. 39

Comparison of the properties of Fluorine with those of Chlorine :

Both Fluorine and Chlorine are gaseous elements ; the colour of Fluorine is pale greenish-yellow, whereas Chlorine is distinctly greenish-yellow in colour. Fluorine is slightly heavier than air (D = 19), where as Chlorine is two-and-a-half times heavier than air. The solubility of Fluorine in water cannot be measured, because it decomposes water with the evolution of ozonised oxygen ; Chlorine, on the other hand, is fairly soluble in water, giving what is known as Chlorine-water.

Fluorine has a very great affinity for Hydrogen and combines with it with explosion even in the dark and at low temperatures with the formation of HF which is stable ; Chlorine combines with Hydrogen readily in direct sun-light with explosion and in diffused light slowly, but not in the dark, with the formation of HCl which is less stable than HF. Fluorine decomposes water at ordinary temperature with the evolution of ozonised oxygen and formation of HF :—$2H_2O + 2F_2 = 4HF + O_2$; $3H_2O + 3F_2 = 6HF + O_3$; Chlorine decomposes water when its aqueous solution is kept exposed to sunlight with the formation of HCl and evolution of oxygen : $2Cl_2 + 2H_2O = 4HCl + O_2$; at 0°C. Chlorine forms a crystalline hydrate, $Cl_2, 10H_2O$ with water.

Fluorine is the most active of the halogen elements and can displace from combination Chlorine, Bromine and Iodine ; Chlorine is less active than Fluorine and can displace only Bromine and Iodine and from combination. Fluorine forms two oxides, F_2O and F_2O_2 by indirect combination with Oxygen, F_2O_2 is unstable at ordinary temperatures ; Chlorine, on the other hand, forms several unstable oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7, by indirect combination with Oxygen. With 2% solution of caustic soda, Fluorine reacts giving fluorine monoxide and sodium fluoride ; with concentrated NaOH solution, Fluorine reacts, evolving oxygen and forming sodium fluoride ; Chlorine, on the other hand, yields sodium hypochlorite and sodium chloride with dilute and cold NaOH solution, whereas with hot and concentrated NaOH solution, it yields sodium chlorate and sodium chloride.

$$2NaOH + 2F_2 = 2NaF + F_2O + H_2O$$
$$4NaOH + 2F_2 = 4NaF + 2H_2O + O_2$$
$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$
$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O.$$

Q. 5. *How are the following substances prepared and what are their uses :—*

(*a*) *Corrosive sublimate ;* (*b*) *bleaching powder ;* (*c*) *potassium chlorate ;* (*d*) *blue vitriol :* (*e*) *red lead ?*

Ans. (*a*) Corrosive sublimate is mercuric chloride, $HgCl_2$. It is prepared by subliming a mixture of mercuric sulphate, common salt and a little manganese dioxide in a long-necked flat-bottomed flask heated on a sand-bath :—

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

The flask is broken after cooling and the cake of sublimate (which is $HgCl_2$) removed from the upper part. MnO_2 is added to prevent the formation of mercurous chloride from mercurous sulphate present usually in mercuric sulphate.

Uses : Mercuric chloride is used in medicine as an antiseptic, and in dressing skins, furs, etc.

(*b*) In modern works, bleaching powder is manufactured with the help of large rotating inclined iron cylinders which are cooled externally by water spray. Slaked lime is fed in at the top and electrolytic chlorine diluted with air is fed in at the bottom. The reaction is vigorous. The temperature is kept below 40°C. The bleaching powder formed is discharged at the bottom and packed in barrels.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Uses : Bleaching powder is used as an oxidising, bleaching and chlorinating agent, as a germicide and for water purification.

(*c*) The most modern method for the preparation of potassium chlorate is by the electrolysis of an aqueous solution of potassium chloride at 80°—90°C. without keeping the cathode and the anode products separate.

The apparatus consists of a lead-lined wooden vessel provided with mechanical stirrers, in which a concentrated solution of KCl, containing a very small amount of HCl, is taken. The *anode* is made of an alloy of Platinum-iridium, while the cathode is of iron or graphite. A little quantity of $K_2Cr_2O_7$ is added to the solution in order to prevent the cathodic reduction of $KClO_3$ produced. Electric current is passed in, when KCl is decomposed. Potassium, liberated at the *cathode*, reacts with water of the solution, giving KOH solution and evolving H_2 which is actually liberated at the cathode ; and Cl_2 is liberated at the anode. The temperature of the solution rises spontaneously which is maintained at about 80°—90°C. Chlorine, liberated at the *anode*, now reacts with hot and conc. KOH solution, giving $KClO_3$ and KCl. The solution is removed and on evaporation, $KClO_3$ being less soluble than KCl, crystallises out. This is filtered off, dried, and recrystallised after being dissolved in the minimum quantity of hot water to get a pure product.

$$\underset{\text{}}{KCl} = \underset{\substack{\text{at the}\\\text{cathode}}}{K} + \underset{\substack{\text{at the}\\\text{anode}}}{Cl}$$

$$2K + 2H_2O = 2KOH + H_2 \text{ (at the cathode).}$$

$$Cl + Cl = Cl_2 \text{ (at the anode).}$$

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Uses : Potassium chlorate is used in the preparation of explosives and in pyrotechny, in the manufacture of matches, for the preparation of oxygen in the laboratory and as an oxidising agent. It is also used in medicine.

(*d*) Blue vitriol or copper sulphate pentahydrate, $CuSO_4$, $5H_2O$, can be obtained by heating metallic copper with conc. H_2SO_4, when SO_2 is evolved and copper sulphate remains in solution.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

After cooling, the solution is carefully decanted off and diluted and filtered. On crystallising the filtrate, blue crystals of $CuSO_4$, $5H_2O$ are obtained.

It is manufactured by roasting copper pyrites, Cu_2S, Fe_2S_3, at such a temperature that Cu_2S is converted into $CuSO_4$ and Fe_2S_3 into Fe_2O_3. After cooling, the roasted mass is extracted with water. The solution is taken off, filtered, concentrated and cooled, when crystals of *blue vitriol*, $CuSO_4$, $5H_2O$, separate out.

Uses : Blue vitriol is used in electroplating, electrotyping and in some electric cells. It is used in dyeing industry. Because of its germicidal action it is used in medicine and in agriculture. A spray of a mixture of copper sulphate and milk of lime is used for killing moulds and fungi in vines and in wheat etc. Anhydrous copper sulphate (white) is used for detecting small amounts of water present in organic liquids.

(*e*) ***Red lead***—Pb_3O_4—It is prepared by roasting lead carbonate (or white lead) or lead monoxide in air for a long time at 400°C.

The heating should not be above 470° since it begins to decompose at 470°C.

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4,$$

Red lead is used as a paint, in the manufacture of flint glass and of matches.

Q. 6. *What is catalysis? Describe one industrial process and one laboratory process, based on the use of a catalyst, for the preparation of important chemical substances.*

Ans. When a substance, by its mere presence, can either accelerate or retard a chemical action, without itself undergoing any change in mass or chemical composition, and a small amount of which can bring about the chemical change in an indefinite amount of the reacting substances, it is said to be a catalytic agent or a catalyst and the *process* is called catalysis. Thus, in the conversion of SO_2 to SO_3 by excess of oxygen, platinum in finely divided state is used. In absence of finely divided platinum, the rate of combination of SO_2 with O_2 is very slow, but at 450°C. in presence of platinised asbestos, the reaction takes place rapidly. At the end the platinum catalyst remains the same in mass and properties.

For application of a catalyst in one industrial process we describe Haber's process of the production of synthetic ammonia by the use of finely divided iron as catalyst with molybdenum as promoter.

Carefully purified nitrogen and hydrogen are mixed in the proportion of 1 : 3 by volume. The mixture is then compressed to 200 atmospheres and is circulated over a catalyst like iron with molybdenum as promoter heated electrically to a temperature of 550°C.—700°C. Under these conditions nitrogen and hydrogen combine to a certain degree giving ammonia which is removed either by liquefaction or by absorption in water.

$$N_2 + 3H_2 = 2NH_3.$$

The remaining nitrogen and hydrogen are recirculated through the system by being pumped back therein and further combination is thereby carried out.

For application of a catalyst in laboratory process, we can mention the use of MnO_2 as catalyst in the preparation of oxygen from potassium chlorate.

A quantity of potassium chlorate is mixed with ¼th of its weight of manganese dioxide and the mixture is placed in a hard glass test tube fitted with a cork and a delivery tube passing through the cork. The hard glass test tube is gently heated when oxygen is evolved. If any spark be seen inside the hard glass test tube, the flame is removed and oxygen comes out in torrents. When the evolution of oxygen is slackened, heating is resorted to.

$$2KClO_3 + [MnO_2] = 2KCl + 3O_2 + [MnO_2].$$

Q. 7. *Name the important minerals in which aluminium occurs. Describe the extraction of the metal and state its uses.*

Explain, giving equations, the action of (a) caustic soda solution, (b) dilute hydrochloric acid and (c) copper sulphate solution on the metal.

Ans. Important minerals containing aluminium are :

(1) *Gibbsite*, Al_2O_3, $3H_2O$
Diaspore, Al_2O_3, H_2O
Bauxite, Al_2O_3, $2H_2O$ (only ore from which Al is extracted).

(2) *Potash-felspar or orthoclase*, K_2O, Al_2O_3, $6SiO_2$, which gives rise to *Kaolin*, Al_2O_3, $2SiO_2$, $2H_2O$ by weathering.

(3) *Cryolite* AlF_3, $3NaF$.

(4) *Alunite*, K_2SO_4, $Al_2(SO_4)_3$, $2Al_2O_3$, $6H_2O$.

(5) *Spienel*, MgO, Al_2O_3.

(6) *Chysoberyl*, BeO, Al_2O_3.

Metallic aluminium is exclusively extracted from bauxite, but since this mineral is contaminated with iron oxide and silica it is first to be purified before it can be utilised for the manufacture of pure aluminium.

The purification is carried out, in case of *red* bauxite containing much iron and less silica, by Bayer's process. Bauxite is first calcined to remove organic matter and then digested with caustic soda solution under pressure and at a temperature of 150°C. Aluminium oxide present in bauxite goes into solution as sodium aluminate and oxide of iron is left behind. The solution of sodium aluminate (containing a little sodium silicate) is separated from precipitated iron oxide and is then agitated with some precipitated alumina from previous operation.

This operation precipitates nearly all the aluminium present in solution as a sandy precipitate of $Al(OH)_3$. This precipitate is filtered, washed, dried and calcined to yield nearly pure alumina :

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O,$$
$$NaAlO_2 + 2H_2O = Al(OH)_3 + NaOH,$$
$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

The alumina so obtained is then dissolved in fused cryolite taken in an iron box lined with block of gas-carbon which is made the cathode. The anodes are carbon rods set in a row inside the bath and placed about 2 to 3 inches above the bottom of the iron box. The box is provided with an outlet pipe at the bottom to take out molten aluminium from time to time. The temperature of the electrolyte is over 900°C. A little fluorspar is added to increase the fluidity of the bath. The molten bath is covered with powdered anthracite in order to prevent the dazzling glow of the bath from reaching the eye. When electric current is passed, alumina undergoes decomposition. Aluminium, liberated at the cathode, sinks in the liquid state to the bottom and forms a pool beneath the anodes. It is taken out from time to time by means of the tap-hole. The oxygen, liberated at the anodes, attacks the carbon of the anodes producing CO and CO_2 in about equal volumes, which are evolved away. The resistance of the electrolyte gives sufficient heat to maintain the temperature at 900°C. and to keep the mass in the fused condition. Fresh Al_2O_3 is added from time to time and the process is continuous. When Al_2O_3 is used up, the resistance of the bath increases and then a lamp, which is shunted off the circuit, brightens. The workmen then understand that fresh Al_2O_3 is to be added.

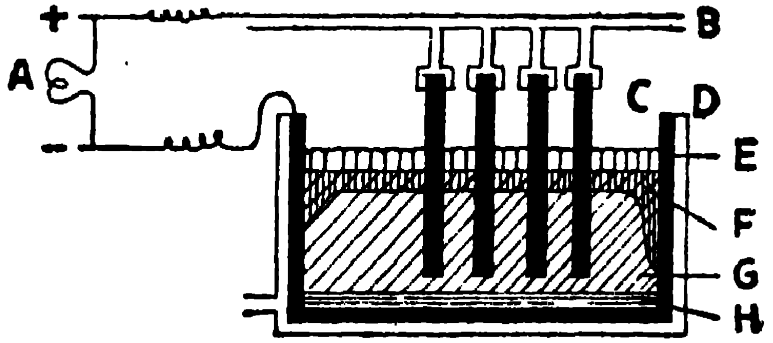


Fig. 40

$$2Al_2O_3 = 4Al + 6O_2$$
$$2C + O_2 = 2CO$$
$$C + O_2 = CO_2.$$

The metal obtained is 99% pure.

Uses of aluminium.—For the extreme lightness of the metal it is largely used for making air-ships and engine-parts. It is also used in the manufacture of utensils, surgical instruments, electric wires and cables (used in U.S.A.). It is used as a reducing agent in the production of Cr, Si, Mn, etc., by Goldschmidt's thermit process, in the manufacture of steel, for making light alloys like magnalium, duralumin, aluminium bronze, etc. It is also added to molten steel during casting in order to prevent formation of blowholes. Al-powder is used as a paint for preserving iron articles against rusting as also in fire-works.

(*a*) A hot solution of caustic soda dissolves aluminium rapidly, forming sodium aluminate and evolving hydrogen gas.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

(*b*) Dilute hydrochloric acid dissolves aluminium in the cold producing aluminium chloride in solution and evolving hydrogen gas.

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

(*c*) Copper is displaced from copper sulphate solution and is deposited as metallic copper and aluminium passes into solution as aluminium sulphate.

$$2Al + 3CuSO_4 = Al_2(SO_4)_3 + 3Cu.$$

Q. 8. *Give reasons why*

(*a*) *dilute sulphuric acid and* **not** *nitric acid is used for the preparation of hydrogen using metallic zinc.*

(*b*) *hydrochloric acid and* **not** *sulphuric acid is used to generate carbon dioxide from limestone.*

(*c*) *sulphuric acid and* **not** *nitric acid is used to prepare hydrochloric acid from sodium chloride.*

(*d*) *lime and* **not** *calcium chloride or sulphuric acid is used to dry ammonia gas.*

(*e*) *dilute sulphuric acid and* **not** *nitric acid is used in Kipp's apparatus for the generation of sulphuretted hydrogen from ferrous sulphide.*

(*f*) *a solution of sodium hydroxide and* **not** *of ammonium hydroxide is used to precipitate mercuric oxide from a solution of mercuric chloride ?*

Ans. (*a*) By the action of dilute nitric acid on zinc, hydrogen may be liberated at first, but it is oxidised as soon as liberated to water by nitric acid which is reduced to nitrous oxide or to ammonia depending on its concentration.

(1) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$

(2) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$.

In the case of dilute sulphuric acid, no such reduction of the acid can take place and hydrogen is obtained in regular supply.

(*b*) Hydrochloric acid generates CO_2 from limestone, $CaCO_3$, and gives rise to $CaCl_2$ which is extremely soluble in water. Thus, the fresh surface of limestone always comes in contact with the acid and the generation of CO_2 continues unhampered. But when sulphuric acid is used, at first CO_2 is evolved and $CaSO_4$ is formed. This $CaSO_4$ is sparingly soluble in water and forms a coating on the surface of limestone. Hence the fresh surface of $CaCO_3$ is prevented from coming in contact with the acid and so the reaction stops. Hence, in generating CO_2 from limestone, hydrochloric acid is preferred to sulphuric acid.

$$CaCO_3 + 2HCl = CaCl_2 \text{ (soluble)} + CO_2 + H_2O.$$

$$CaCO_3 + H_2SO_4 = CaSO_4 \text{ (sparingly soluble)} + CO_2 + H_2O.$$

(*c*) (*i*) HNO_3 being more volatile than H_2SO_4, there is every chance of it passing with the vapours of HCl into the receiver.

(*ii*) As soon as HNO_3 comes in contact with HCl which is evolved during the reaction, it oxidises HCl with the formation of chlorine which is evolved as a greenish yellow gas. $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$. So HNO_3 is not used in the preparation of HCl from NaCl.

(*d*) Quicklime, CaO, is a basic substance, just like ammonia. So ammonia does not react with lime, only the moisture present in ammonia is taken up by quicklime with the production of slaked lime.

$$CaO + H_2O = Ca(OH)_2.$$

But ammonia is absorbed by fused calcium chloride with the production of $CaCl_2, 8NH_3$.

$$CaCl_2 + 8NH_3 = CaCl_2, 8NH_3.$$

Also ammonia, a base, reacts with sulphuric acid (conc.), an acid, with the production of the salt ammonium sulphate and hence no ammonia will be left over.

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4.$$

So the gas will be absorbed both by $CaCl_2$ and by conc. H_2SO_4.

(*e*) Nitric acid is *not* used in Kipp's apparatus for generating sulphuretted hydrogen from ferrous sulphide for the following reasons :—

(*i*) Nitric acid is a volatile acid and so when H_2S is evolved, it sweeps out a little quantity of nitric acid vapour along with it and thus H_2S will be contaminated with nitric acid vapour.

(*ii*) Nitric acid will bring about oxidation of H_2S evolved with separation of S and this S in its turn will be oxidised by nitric acid to SO_2. Nitric acid itself will be reduced to NO_2 and this NO_2 will get mixed up with any H_2S which may escape oxidation. Moreover, ferrous sulphide also is oxidised to a certain extent to ferrous sulphate. Thus, much nitric acid is wasted.

Primary reaction is $FeS + 2HNO_3 = Fe(NO_3)_2 + H_2S$.

Then the secondary reactions set in.

$$H_2S + 2HNO_3 = 2H_2O + 2NO_2 + S.$$

Also,

$$FeS + 4HNO_3 = FeSO_4 + 2H_2O + 2NO + 2NO_2.$$

(*iii*) Sulphuric acid is preferred to nitric acid from the view-point of cost, sulphuric acid, being less costly, is used in this case.

(*f*) By the action of sodium hydroxide solution on a solution of mercuric chloride, yellow oxide of mercury, HgO, is precipitated.

$$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl.$$

(Here it is to be noted that no hydroxide of murcury is known.)

But by adding ammonium hydroxide to a solution of mercuric chloride, a white precipitate of amido-mercuric chloride, NH_2HgCl, known as *infusible white precipitate*, is obtained instead of yellow oxide of murcury.

$$HgCl_2 + NH_4OH = NH_2HgCl + HCl + H_2O.$$

So ammonium hydroxide is never used for getting mercuric oxide from a solution of mercuric chloride.

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SECOND PAPER

Q. 1. *0'0321 gram of an impure sample of aluminium gave on treatment with dilute hydrochloric acid 39'3 c.c. of moist hydrogen measured at 13°C. and 761 m.m. pressure. The impurity in the sample was alumina. Calculate the percentage of purity of the metal.*

[At. wt. of Al = 27, Aq. Tension at 13°C = 11 mm.]

Ans. The pressure of *dry* hydrogen (761 − 11) mm. = 750 mm.

Let V c.c. be the volume of *dry* hydrogen at N.T.P.

Then by Boyle's and Charles' Laws, we have

$$\frac{39'3 \times 750}{273+13} = \frac{V \times 760}{273}$$

$$\therefore \quad V = \frac{39'3 \times 750 \times 273}{286 \times 760} \text{ c.c.}$$

$$= 37'02 \text{ c. c.}$$

Now, from the equation

$$\underset{2\times 27}{2\text{Al}} + 6\text{HCl} = 2\text{AlCl}_3 + \underset{3\times 2}{3\text{H}_2}$$

we know that 3 × 2 grams of hydrogen can be obtained by the use of 2 × 27 grams of aluminium. Since molecular weight of any gas expressed in grams occupies 22'4 litres at N.T.P. therefore 3 × 22'4 litres of hydrogen at N.T.P., can be obtained by the use of 2 × 27 grams of aluminium.

Hence in order to obtain 37'02 c. c. of hydrogen at N.T.P. the amount of aluminium required

$$= \frac{2 \times 27 \times 37'02}{3 \times 22'4 \times 1000} \text{ gram.}$$

$$= 0'02975 \text{ gram.}$$

Therefore 0'0321 gm. of impure sample of aluminium contained 0'02975 gm. of pure aluminium.

∴ pure aluminium present in the sample

$$=\frac{0{\cdot}02975}{0{\cdot}0321}\times 100\% = 92{\cdot}68\%.$$

Q. 2. *Mention at least* **one** *reaction in* **each** *of the following cases to show that nitric acid, sulphuric acid, chlorine and hydrogen peroxide are all oxidising agents.*

Explain carefully the tests, to show that oxidation has actually occurred in the cases you mention.

Ans. Nitric acid as an oxidising agent :—

Concentrated hydrochloric acid is mixed with concentrated nitric acid in the proportion of 3 : 1 by volume and the mixture heated. Chlorine gas is evolved, which is recognised by its greenish-yellow colour, smell like that of bleaching powder and its power to turn starch-iodide paper blue.

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O.$$

Hence hydrochloric acid is oxidised to chlorine by removal of hydrogen and nitric acid is reduced to nitrosyl chloride. Nitric acid, therefore, has oxidised hydrochloric acid to chlorine.

Sulphuric acid as an oxidising agent :—

Solid potassium bromide is heated with concentrated sulphuric acid when bromine vapour is evolved, recognised by its brown colour, peculiar smell and its capability to turn starch-iodide paper blue.

$$2KBr + 3H_2SO_4 = 2KHSO_4 + Br_2 + SO_2 + 2H_2O.$$

Bromine is an oxidation product of potassium bromide, as it is produced from potassium bromide by the removal of electro-positive element potassium. Also at the same time sulphuric acid is reduced to sulphur dioxide.

Hence sulphuric acid has oxidised potassium bromide to bromine.

Chlorine as an oxidising agent :—

Thin leaves or foils of copper (or *Dutch metal*) are introduced into a jar of chlorine. The leaves burn spontaneously in the gas and green deposit is obtained in the gas-jar. It is of cupric chloride.

$$Cu + Cl_2 = CuCl_2.$$

That it is cupric chloride is proved by dissolving the green deposit in water and adding silver nitrate solution to it. A curdy white precipitate is formed, insoluble in HNO_3 but soluble in NH_4OH. Hence an electro-negative element chlorine is added to copper and therefore oxidation of copper has taken place with the help of chlorine.

Therefore, chlorine must have oxidised copper to cupric chloride.

Hydrogen peroxide as an oxidising agent :—

When dilute sulphuric acid is added to potassium iodide solution, no iodine is liberated ; but this acidified solution of potassium iodide, when treated with a solution of hydrogen peroxide, liberates iodine which is proved by the fact that it turns starch solution blue.

$$2KI + H_2SO_4 + H_2O_2 = K_2SO_4 + 2H_2O + I_2.$$

Iodine is an oxidation product of potassium iodide, since an electro-positive element potassium is removed from potassium iodide. Hydrogen peroxide is reduced to water.

Thus hydrogen peroxide oxidises potassium iodide to iodine.

Q. 3. *Compare and contrast the flames produced by burning marsh gas alone and also mixed with air. Explain the reactions that take place in the different zones of the flame.*

What happens when methane mixed with chlorine is (a) exposed to diffused day-light and (b) ignited ? Give equations to illustrate your answer.

Ans. When marsh gas is burnt alone in air in a jet as in a Bunsen burner, with its air-hole closed, it burns with a luminous flame.

The flame usually consists of 4 zones :

(1) *The zone of no combustion.*—Here very little chemical change occurs and unburnt gas is present here. It is dark in colour.

(2) There is a small region at the base of the flame which appears bright blue in colour and is *non-luminous*.

Here some carbon monoxide produced by insufficient oxidation undergoes combustion.

(3) Above the zone of no combustion we have the *luminous*

middle zone of incomplete combustion. Here the gas is partially oxidised to carbon monoxide and partial combustion of carbon monoxide and hydrogen takes place here, with separation of carbon particles. The luminosity of this zone is due to the incandescence of these solid particles of C.

(4) Then comes the faintly luminous outermost zone. It surrounds the entire flame and may be termed the *zone of complete combustion.*

Since the supply of oxygen here is quite sufficient, carbon monoxide, hydrogen, solid particles of C. etc., escaping combustion in the luminous zone, are fully oxidised. The final products are carbon dioxide and steam.

When marsh gas is mixed with air and is set fire to for making it burn, it explodes.

But when it is burnt in a jet, as in a Bunsen burner with the air-hole gradually opened, the gas, coming out of the *jet*, and passing unburnt up the tube, sucks in air through the air-hole and burns at the mouth of the burner tube. The flame becomes non-luminous and shorter in size. It now consists practically of *two zones only* :—(1) the inner blue zone, the region of unburnt gas and (2) the outer non-luminous zone of complete combustion.

If the air-hole be completely opened, the flame roars and then it sinks and travels downwards and the marsh gas begins to burn at the *jet.* Then the flame is said to *strike back.* Acetylene is produced in large quantities and the burner tube becomes very hot under these conditions.

(*a*) When methane is mixed with chlorine and exposed to diffused daylight, substitution of hydrogen by chlorine takes place atom by atom and hydrogen chloride is generated. Different substitution products are obtained, depending upon the quantity of chlorine and time of exposure :—

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

Methyl chloride

$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$$

Methylene chloride

$$CH_2Cl_2 + Cl_2 = CHCl_3 + HCl$$

Chloroform

$$CHCl_3 + Cl_2 = CCl_4 + HCl$$

Carbon tetrachloride

(b) When the mixture of methane and chlorine is ignited, it explodes with the formation of hydrogen chloride and separation of carbon in the form of soot.

$$CH_4 + 2Cl_2 = C + 4HCl.$$

Q. 4. *Bottles A, B, C, D, E, are known to contain potassium iodide, magnesium nitrate, ammonium sulphate, potassium chloride and calcium hydroxide. How will you find which is which ?*

Ans. A little of each of these substances is taken on a clean Pt-wire previously rinsed with conc. HCl, then dipped in conc. HCl and heated in the non-luminous flame of the Bunsen burner by holding the Pt-wire at the base of the flame and then gradually raising it up.

That substance which imparts a transient brick-red coloration to the flame is the calcium compound and it is calcium hydroxide, seeing that there is no other calcium compound present. It is further confirmed by acidifying a clear solution of the substance with acetic acid and then adding ammonium oxalate solution when a white precipitate of calcium oxalate, insoluble in acetic acid, is obtained. Moreover, the solution turns red litmus blue, proving that it is alkaline.

Next, it is found that two of the remaining substances impart a pale violet colour to the flame, which appears red when viewed through double blue glass. These two are potassium compounds. To know which is which, a pinch of each is mixed with MnO_2 and conc. H_2SO_4 and heated. That which evolves violet vapours of iodine is potassium iodide since there is no other iodide in the list and potassium has been identified by flame test before. To further confirm it, a little of this substance is dissolved in water and silver nitrate solution is added to it. A distinctly yellow ppt. insoluble in HNO_3 as well as in NH_4OH is obtained. This ppt. is of silver iodide, AgI.

Next, the substance from which greenish yellow chlorine gas, recognised by its colour and smell, and by its action on starch-iodide paper (which turns blue by its action), is evolved by the above treatment, is potassium chloride since there is no other chloride in the list and the presence of potassium has been confirmed by flame test before. To further confirm it to be a chloride, a little of this substance is dissolved in water and silver nitrate solution is added to it. A curdy white precipitate, insoluble in HNO_3 but soluble in dilute NH_4OH, is obtained. The precipitate is of silver chloride, AgCl.

Of the remaining two, a little of each is taken in a test tube and caustic soda solution is added to it and heated. That which gives smell of ammonia is ammonium sulphate, seeing that no other ammonium compound is present in the list. To further confirm it, a little of the substance is added to Nessler's solution ; either a brown coloration or a brown ppt. depending upon the amount of ammonium salt added, is obtained. Further, when barium chloride solution is added to a solution of this substance, a white precipitate, insoluble in HCl, is obtained, proving the presence of a sulphate.

The remaining substance must be magnesium nitrate. To confirm it, a little of the substance is dissolved in water in a test tube and to the solution so obtained a freshly prepared ferrous sulphate solution is added and then by holding the test tube in a slanting position under a running tap, conc. H_2SO_4 is poured down the test tube. A brown ring is found to be developed at the junction of the two liquids. To another portion of the solution of this substance, ammonium chloride, ammonia, and disodium hydrogen phosphate are added and the mixture is well shaken when a crystalline white precipitate of magnesium ammonium phosphate is obtained, proving the presence of magnesium.

Q. 5. *Write explanatory notes on the reactions that take place when :—*

(*a*) *sodium is placed into an aqueous solution of caustic soda,*

(*b*) *iron is dipped into concentrated and dilute nitric acid separately,*

(*c*) *zinc dust is sprinkled into a solution of copper sulphate.*

(*d*) *aluminium is dipped into mercuric chloride.*

Give equations wherever you can.

Ans. (*a*) Here sodium reacts with water present in caustic soda solution producing sodium hydroxide and evolving hydrogen gas.

$$2Na + 2H_2O = 2NaOH + H_2.$$

So ultimately the concentration of caustic soda solution increases.

(*b*) When iron is dipped into very concentrated nitric acid, it is rendered passive *i.e.*, it loses the property of dissolving in dilute acid and its capability of displacing copper from copper sulphate solution.

But with ordinary concentrated nitric acid, iron reacts, forming ferric nitrate and giving chiefly nitrogen peroxide.

$$Fe + 6HNO_3 = Fe(NO_3)_3 + 3H_2O + 3NO_2.$$

With dilute nitric acid iron reacts, forming ferrous nitrate and ammonium nitrate.

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 3H_2O + NH_4NO_3.$$

(*c*) Here displacement reaction takes place. Zinc displaces copper from copper sulphate solution and this copper is precipitated whereas an equivalent amount of zinc passes into solution as zinc sulplate.

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

(*d*) If a piece of aluminium be dipped into solid mercuric chloride and the adhering $HgCl_2$ be rubbed, a deposit of Hg on aluminium surface occurs, the surface becomes very hot and ultimately excrescences of Al_2O_3 appear on the surface due to oxidation of Al-amalgam.

But when aluminium is dipped into mercuric chloride solution, displacement of mercury takes place which forms aluminium amalgam and an equivalent quantity of aluminium passes into solution as aluminium chloride, $AlCl_3$.

$$2Al + 3HgCl_2 = 3Hg + 2AlCl_3.$$

Al amalgam is also called aluminium-mercury couple and it has the capacity of decomposing water in the cold evolving hydrogen.

Q. 6. *How is pure copper isolated from copper pyrites? Describe the method in detail, making it clear how other metals are removed from the ore in course of the process. Represent the reactions involved by equations.*

How are cuprous chloride and cupric oxide prepared? State their uses.

Ans. Pure copper from copper pyrites Cu_2S, Fe_2S_3, is obtained by a thermal process, the copper produced being subsequently purified by electrolysis.

At first the ore is concentrated either by gravity separation or by Floatation process. For operating the latter method, the ore is first crushed and finely powdered. The powdered ore is next churned with water containing a little pine oil and lime, by blowing air through it. By this operation a froth is produced, which carries up along with it the particles of copper ore, leaving sand and other impurities at the bottom of the vessel. The froth is collected by skimming and allowed to settle.

The concentrated ore is next roasted in a multiple hearth furnace, whereby excess of sulphur present is burnt out to SO_2 and the metals, *viz.*, Fe present in pyrites and copper are partially oxidised.

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$

The second reaction occurs only to a very small extent. The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when a little quantity of Cu_2O formed in the previous operation of roasting reacts with iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced in the previous operation, reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained in the molten state is a mixture of cuprous and ferrous sulphides and goes by the name of *copper matte.* The molten matte is then directly run into a Bessemer Converter with a little sand and a blast of air is introduced through tuyeres placed at the sides a little above the bottom level. Iron is first oxidised to FeO which combines with silica forming a slag of ferrous silicate as before. Most of the iron present in the ore is thus removed. The slag is removed from the top and the blast continued. Cu_2S is then partially oxidised to Cu_2O and when about two-thirds of Cu_2S is thus oxidised, the remaining Cu_2S reacts with Cu_2O to form metallic copper and sulphur dioxide.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

The slag is removed, the blast stopped and the converter tilted to pour off copper. This copper has a blistered appearance due to escape of SO_2 and is known as "blister copper."

Blistered copper is then melted on the hearth of a reverberatory furance in a current of air when the metallic and non-metallic impurities like Fe, Pb, Bi, S, As, etc. are oxidised. Some of the oxides escape as gas, others form a slag with silica lining of the furnace (known as refinery slag). The slag is removed. A small amount of cuprous oxide is also formed, which remains dissolved in the copper. In order to remove that cuprous oxide, powdered anthracite coal is sprinkled on the surface of the molten mass and the mass of copper is stirred with a pole of green wood thurst into the molted metal. Torrents of reducing hydrocarbon gases bubble up through the metal and cuprous oxide is reduced thereby. When the copper attains the requisite *tough pitch*, as judged from the appearance of the fractured surface, it is poured out of the furnace. Here also base metals like Fe, Bi, Pb, etc. are removed. But the precious noble metals like gold and platinum present in the copper pyrites are not removed here. These are collected as anode-mud during the electrolytic refining of copper, by which 99·96% pure copper is obtained.

Thick blocks of impure copper are made the anodes in a bath of copper sulphate solution, acidified with 15% of sulphuric acid, taken in a vessel. Thin sheets of pure copper are made the cathodes, anodes and cathodes being alternately suspended in the bath from two rods connected to the positive and negative poles of a battery respectively. Copper dissolves at the anode as cupric ions, which travel to the cathode. These cupric ions give up their charges at the cathode and are deposited there as pure copper. Base metals like iron, arsenic, zinc etc. pass into solution and precious metals along wiih lead collect round the anode as *anode slimes.*

Cuprous chloride, CuCl.

Cupric oxide, CuO, is taken in a small flask and treated with excess of concentrated HCl. The solution is then boiled with copper turnings. When the reaction is over, the liquid is poured into a large volume of water. A white precipitate of cuprous chloride is obtained. It is filtered and dried.

$$CuO + 2HCl = CuCl_2 + H_2O$$

$$CuCl_2 + H = CuCl + HCl \quad | \quad Cu + CuCl_2 = 2CuCl.$$

Cuprous chloride is a white crystalline solid. It is insoluble in water and in dil. HCl. But it dissolves in conc. HCl and in NH_4OH giving a colourless solution. But the HCl-solution rapidly turns green and the ammoniacal solution blue on exposure to air, due to oxidation.

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O.$$

The ammoniacal solution of cuprous chloride readily absorbs oxygen, carbon monoxide and acetylene. With acetylene a red precipitate of cuprous acetylide, Cu_2C_2, H_2O is formed. When heated it first melts and then volatilises away as such.

Ammoniacal solution of cuprous chloride is used in gas analysis for removal by absorption of carbon monoxide, or oxygen or acetylene from a gas mixture.

Cupric oxide, CuO.

Cupric oxide is prepared by heating cupric nitrate strongly in air. Black powdery cupric oxide is obtained by this means.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

Uses of CuO : (1) in analysis, both qualitative and quantitative, of organic compounds ;

(2) in glass manufacture, for imparting blue colour to glass.

Q. 7. *What are the processes for the manufacture of sodium carbonate ? Describe any one process and indicate the relative merits of the different processes.*

Ans. There are *three* processes now in vogue :—

(*i*) Leblanc's process, (*ii*) Solvay or Ammonia soda process and (*iii*) Electrolytic or Hargreaves-Bird process.

Ammonia-soda process or Solvay's process is now mostly employed for the manufacture of sodium carbonate. This process is based upon the reaction between hydrogen ammonium carbonate (produced by the action of carbon dioxide on ammonia solution) and a strong solution of sodium chloride according to the equation

$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3.$$

The bicarbonate of sodium so produced is precipitated out, collected, and then calcined to yield sodium carbonate :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The actual operation is carried out as follows :—

Brine directly obtained from salt-beds by pumping in water into the salt-beds and then pumping out the sodium chloride solution so produced, is saturated with ammonia gas in towers and the ammoniated brine is cooled. Next in carbonating towers, this ammoniated brine is treated with carbon dioxide gas obtained from lime-kilns where quicklime is produced from limestone by heating :—

$$CaCO_3 = CaO + CO_2.$$

Carbon dioxide is passed up the tower under moderate pressure, down which the ammoniated brine trickles through perforated baffle plates.

Carbon dioxide reacts with ammonia first, giving rise to ammonium bicarbonate :

$$CO_2 + NH_3 + H_2O = NH_4HCO_3.$$

The bicarbonate of ammonium then reacts with sodium chloride forming sodium bicarbonate and ammonium chloride by double decomposition :

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

This sodium bicarbonate being sparingly soluble separates out in the solid state, leaving more soluble ammonium chloride in solution. The above reaction takes place most efficiently between 30° – 40°C., and hence there is cooling arrangement in the carbonating tower. Sodium bicarbonate, which has separated out near the perforations in the baffle plates is collected and calcined in iron pans to get sodium carbonate.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$

In this operation CO_2 is produced which is utilised in carbonating towers. Ammonia is recovered from ammonium chloride solution by heating with quicklime produced in lime kilns and is used in ammoniating the brine.

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O,$$

So the process is self sufficient.

Only there is an working loss of about 2% of ammonia and this is to be replaced from time to time.

In the Leblanc process HCl is obtained as a by-product from the absorption towers and is supplied to the market as commercial HCl. Sulphur is recovered from the waste CaS, obtained from lixiviating tanks, known as Alkali-maker's waste. Na_2SO_4, obtained in the first operation by heating NaCl with conc. H_2SO_4, and known as salt-cake, is used in the manufacture of glass. On account of the commercial utilisation of these by-products Leblanc process, though costly in comparison with the other methods, still holds its own.

Solvay's process or Ammonia soda process is cheaper than Leblanc process since sodium chloride is used as brine directly from salt-bed and limestone used to get CO_2 and lime is obtained very cheap. Also NH_3 and CO_2 are obtained as by-products and are used over and over again. The product obtained is pure and the intermediate product, sodium bicarbonate, finds direct application in medicine and in other directions. The operation of the process is free from evolution of any obnoxious vapours.

The electrolytic or Hargreaves-Bird process is the cheapest of the three processes, specially where electricity is obtained from water-power. The product sodium carbonate is very pure. Chlorine and hydrogen are obtained as very important by-products, since chemically pure HCl is prepared now exclusively by burning these two gases in a special burner.

1947

FIRST PAPER

Q. 1. *Enunciate Avogadro's hypothesis and show how it leads to a clear interpretation of Gay-Lussac's law of gaseous volumes.*

How would you prove that a molecule of hydrogen consists of two atoms and that the density of any gas is half its molecular weight ?

Ans. Avogadro's Hypothesis :—Equal volmes of all gases and

vapours whether elementary or compound, contain identical number of molecules under the same conditions of temperature and pressure.

Gay-Lussac experimentally established that when gases combine among themselves, they do so in simple numerical proportion by volume and the volumes of the reacting gases bear a simple relation to the volume of the resulting product, if that be gaseous, the volumes being all measured under the same conditions of temperature and pressure. Thus it is found by Gay-Lussac that 1 volume of hydrogen combines with 1 volume of chlorine and forms two volumes of hydrochloric acid gas. By the application of Avogadro's Law, if *n* be the number of molecules present in each volume, we see that *n* molecules of hydrogen combine with *n* molecules of chlorine to form 2*n* molecules of hydrochloric acid gas. That is, 1 molecule of hydrogen combines with 1 molecule of chlorine, giving rise to 2 molecules of hydrochloric acid gas. But every molecule of hydrogen chloride must contain at least one hydrogen and one chlorine atom. Therfore 2 molecules of hydrogen chloride must contain 2 atoms of hydrogen and 2 atoms of chlorine. These 2 atoms of hydrogen must have come from 1 molecule of hydrogen and 2 atoms of chlorine have come from 1 molecule of chlorine. Avogadro pointed out the difference between the atoms and molecules by saying that the free particles of any kind of matter, elementary or compound, which exist in the free state retaining all the properties of that kind of matter are the molecules of that kind of matter, whereas atoms are the smallest particles of elementary matter, which can take part in chemical reaction. With this difference borne in mind, we can easily see that Gay-Lussac's law of gaseous volumes finds a ready explanation from Avogadro's law. All that is necessary is to suppose that hydrogen and chlorine molecules are formed by the union of two atoms of hydrogen and of chlorine respectively.

That a molecule of hydrogen consists *at least* of two atoms of hydrogen is proved from the experimentally determined volume relationship existing between the volumes of hydrogen, chlorine and hydrogen chloride as shown before.

Now, hydrogen present in the molecule of hydrochloric acid gas can be replaced by a metal like sodium in *one instalment* only, giving a normal salt ; and in no case, in more than one, instalment. So we are led to believe that a molecule of hydrogen chloride contains 1 atom of hydrogen. Hence it follows from what has been stated before that 1 molecule of hydrogen consists of two atoms.

(3) *Molecular weight of any gas is twice its density (referred to Hydrogen).*

The density of any gas with respect to Hydrogen is the ratio of the weight of a certain volume of that gas to the weight of the same volume of hydrogen both measured at the same temperature and pressure. Let D be the density relative to Hydrogen of any gas. Then, by definition, we have

$$D=\frac{\text{wt. of } V \text{ vols. of the gas}}{\text{wt. of } V \text{ vols. of Hydrogen}} \quad \text{(under the same conditions of temp. and pressure).}$$

Let "n" be the number of molecules present in V vols. of the gas. Then, by Avogadro's hypothesis, we get

$$D=\frac{\text{wt. of "}n\text{" molecules of the gas}}{\text{wt. of "}n\text{" molecules of Hydrogen}}$$

$$=\frac{n\times\text{wt. of 1 molecule of the gas}}{n\times\text{wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 2 atoms of Hydrogen}} \quad \text{(since Hydrogen molecule is diatomic as proved before).}$$

$$=\frac{\text{wt. of 1 molecule of the gas}}{2\times\text{wt. of 1 atom of Hydrogen}}$$

Hence, $$2\times D=\frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 atom of Hydrogen}}$$

$$=\text{Molecular wt. of the gas (by definition),}$$

Q. 2. *Describe experiments by which you can determine the volumetric composition of steam and the empirical formula for water molecule.*

How and under what conditions does water react with : (a) iron, (b) carbon, (c) calcium carbide? Name the products formed and give equations.

Ans. *Volumetric composition of steam.*

One $\breve{U}$-shaped eudiometer tube with one limb closed and graduated is taken. The closed end of the tube has two platinum wires sealed into the glass. The closed limb is surrounded by a jacket through which amyl alcohol vapour (B. P. 132°C.) can be circulated when required. The other limb of the eudiometer tube is open and it is provided with a side-cock near the bottom.

The closed limb of the U-shaped eudiometer tube is then first filled with mercury and then partially filled with a dried mixture of 2 volumes of hydrogen and 1 volume of oxygen (obtained by the electrolysis of acidulated water and dried by conc. H_2SO_4) by the displacement of mercury. Vapour of amyl alcohol obtained by boiling amyl alcohol in a flask as shown in the figure is then made to circulate through the jacket and this passage of amyl alcohol vapour is continued upto the end of the experiment. Then after some time, when the temperature of the mixed gases becomes constant, the mercury level in both limbs is adjusted to the same height and the volume of the mixture is carefully read off. Some mercury is then run out by opening the tap to reduce the pressure and an electric spark is passed through the gas mixture by connecting the two platinum wires sealed to the closed limb to the terminals of an induction coil after closing the open limb by the thumb. Hydrogen and oxygen combine to produce steam. Mercury level is again adjusted in both the limbs and the volume noted carefully. It will be found that the steam produced is exactly two-thirds of the volume of the mixture of H_2 and O_2 taken.

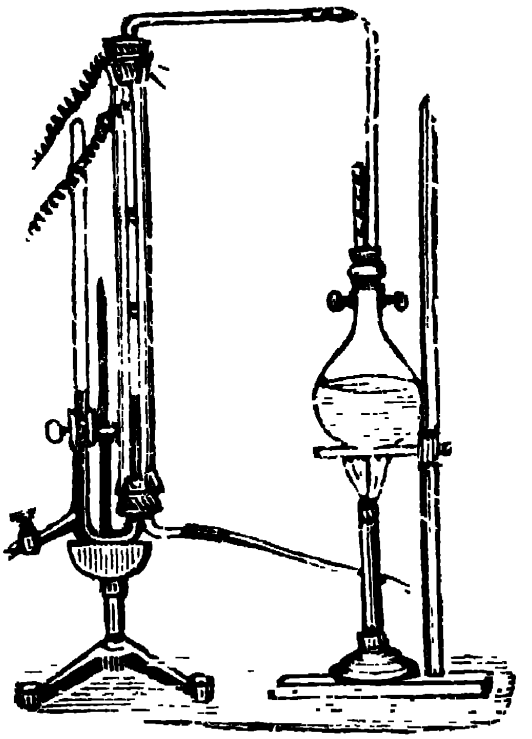


Fig. 41

From the experiment, we know that 2 vols. of H_2 combine with 1 vol. of O_2 to give two volumes of steam.

Let '*n*' be the number of molecules present in 1 vol. of oxygen.

Then, by Avogadro's hypothesis,

$2n$ molecules of hydrogen combine with n molecules of oxygen to form steam (water in the gaseous state) ;

or, 2 molecules of hydrogen combine with 1 molecule of oxygen to form water.

Since, hydrogen and oxygen molecules are diatomic (Avogadro's hypothesis) we find that, 4 atoms of hydrogen combine with 2 atoms of oxygen to form water ;

or, 2 atoms of hydrogen combine with 1 atom of oxygen to form water.

Thus, the empirical formula for water is H_2O, and the molecular formula is $(H_2O)x$, where x is an integer. In order to determine x we require the density of water, but it is known only that in the gaseous state the density of water (*steam*) is 9, whence the molecular formula for steam is H_2O, since it corresponds with the molecular weight of steam, $2 \times 9 = 18$. But density of liquid water is not known and hence its *empirical* formula is accepted as H_2O.

(a) When water in the form of steam is passed over red-hot iron, hydrogen gas is produced and iron is oxidised to ferroso-ferric oxide.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

(*b*) When water in the form of steam is passed over white-hot carbon, a mixture of two gases, carbon monoxide and hydrogen, known as *water gas* is produced.

$$C + H_2O = CO + H_2 \text{ (at and above 1000°C.).}$$

But the above reaction being highly endothermic, the temperature gradually falls and at about 600°C., a mixture of CO_2 and H_2 is obtained.

$$C + 2H_2O = CO_2 + 2H_2 \text{ (at 600°C).}$$

At intermediate temperatures, mixture of CO, CO_2 and H_2 is obtained.

(*c*) Water reacts with calcium carbide in the cold, giving acetylene gas and forming calcium hydroxide.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Q. 3. *How would you prepare an aqueous solution of pure hydrobromic acid in the laboratory ? Give a neat sketch of the apparatus and equations for the reactions that occur.*

Compare the properties of hydrobromic acid with those of hydrochloric acid.

Ans. Hydrobromic acid is prepared in the laboratory by the action of bromine on a mixture of red phosphorus and water.

In a flask fitted with a dropping funnel and a delivery tube, a mixture of red phosphorus and water is taken. The end of the delivery tube is connected with a U-tube containing glass beads with moist red phosphorus to absorb any bromine vapour that may escape from the flask. Then bromine is gradually added from dropping funnel. Hydrobromic acid gas is given off, mixed with Bromine vapours. As the mixture passes through the U-tube, Bromine vapours are absorbed by moist red phosphorus. Hydrobromic acid gas passes on and can be collected by the upward displacement of air. The flask is to be *gently heated* towards the end of the reaction for liberating all the hydrobromic acid vapour.

If a solution of hydrobromic acid is to be prepared, the delivery tube is attached to the stem of a funnel the mouth of which is just dipped under the surface of water contained in a beaker. This arrangement prevents back suction. (See Fig. 10, p. 46)

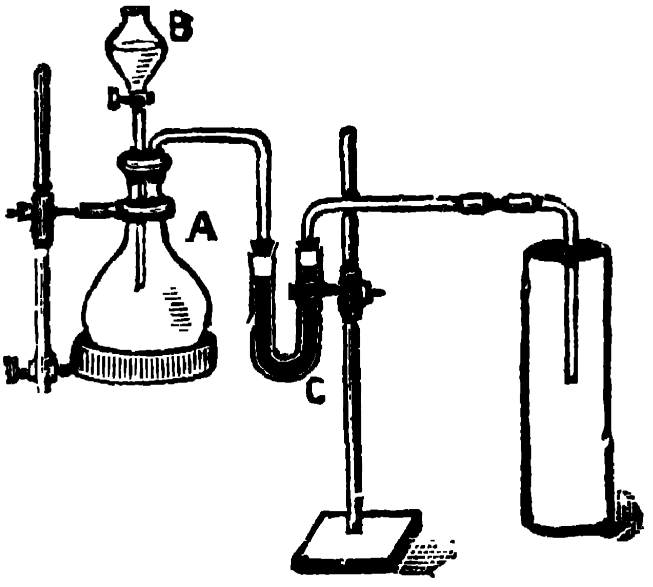


Fig. 42

$$4P + 10Br_2 = 4PBr_5 \ : \ PBr_5 + 4H_2O = 5HBr + H_3PO_4$$

$$4P + 6Br_2 = 4PBr_3 \ : \ PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

Comparison of HBr with HCl and HI.

These compounds, the hydracids of the halogen elements Cl_2, Br_2, and I_2, are all colourless gases which fume strongly in moist air. They are all extremely soluble in water and are strongly acid in character. Of these HCl is the most stable. HBr is decomposed by heat and HI is decomposed by slight heat. They can be distinguished by the following reactions :—

Experiment	HCl	HBr	HI
1. Heated with conc. H_2SO_4.	No coloured vapour, only colourless HCl vaporises away	Brownish—red vapours of Bromine given off.	Violet vapours of Iodine given off.
2. $AgNO_3$ solution is added.	*Curdy-white ppt.* of AgCl produced, insoluble in conc. HNO_3 but soluble even in dil. NH_4OH,	*Yellowish-white ppt.* of AgBr obtained, insoluble in conc. HNO_3, but soluble with difficulty in NH_4OH.	*Yellow ppt.* of AgI produced, insoluble both in conc. HNO_3 and in NH_4OH.
3. Chlorine water with carbon disulphide is added and shaken.	No change in colour of CS_2 layer settling at the bottom.	CS_2—layer at the bottom is coloured *brown.*	CS_2—layer at the bottom is coloured *violet.*
4. Chlorine-water along with starch solution is added.	No change in colour.	Solution turns *orange-yellow* in colour.	Solution becomes *blue* in colour.

Q. 4. *Starting from calcium phosphate describe how you would obtain yellow and red phosphorus. Compare their properties and describe experiments to prove that they are different modifications of the same element. State their uses.*

Ans. Finely ground phosphate of calcium, obtained as rocky matter in nature, is mixed with fine sand and powdered anthracite. The mixture is then fed into an electric furnace lined inside with refractory bricks. The furnace is fitted with a hopper at the top through which the feeding is carried out and the supply of the mixture to the furnace is regulated by an Archimedian screw set beneath the hopper. There is an outlet near the top for the escape of hot gases and vapours of phosphorus, and another at the bottom for taking out the slag. A high temperature is produced near the base by striking an electric arc with the help of two carbon electrodes. At this temperature calcium phosphate will react with silica present in sand, forming calcium silicate, which is a fusible slag.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

The carbon present in the charge reduces the phosphorus pentoxide to phosphorus ;

$$P_2O_5 + 5C = 2P + 5CO.$$

Phosphorus vapour and carbon monoxide are led into water where phosphorus vapour is condensed to solid yellow (white ?) phosphorus and carbon monoxide gas escapes. Calcium silicate is tapped off from time to time. This process is continuous.

Yellow phosphorus is changed to red phosphorus by heating it in a covered vessel provided with a safety valve, with a trace of iodine to 230° – 250°C. Any oxygen which is present at the start is quickly removed by the burning of a little phosphorus. Thereafter heating takes place in an atmosphero of nitrogen. Any unchanged yellow phosphorus is removed by boiling the red material formed with caustic soda solution. The product is thencooled, filtered, washed thoroughly with water and dried.

Comparison of properties of yellow and red P :—

	Property	Yellow P	Red P
1.	Colour.	Almost colourless.	Violet red.
2.	Smell.	Garlic smell	Odourless.
3.	Specific gravity.	1'83	2'05—2'39
4.	Melting point.	44°C.	500°—600°C.
5.	Action of CS_2, chloroform etc.	Readily soluble	Insoluble.
6.	Reaction when exposed to air.	Phosphoresces with glow and oxidation.	Does not phosphoresce (there is no glow and no oxidation).
7.	Ignition temp.	30°C.	240°C.
8.	Hot NaOH sol.	Readily reacts with hot NaOH sol. giving off PH_3.	No action.
9.	Chemical activity.	Highly active.	Less active than yellow P.
10.	Physiological action.	Highly poisonous.	Not poisonous.
11.	Stability.	Less stable at ordinary temperature.	Stable at ordinary temperature.

Experiments to show that yellow P and red P are different modifications of the same element :—

(1) Equal weights of yellow P and red P are taken and burnt carefully in excess of oxygen by suitable arrangement and the products collected and dissolved in excess of water, whereby phosphoric acid, H_3PO_4 is formed. These two different solutions are neutralised and completely precipitated separately with magnesia mixture in presence of ammonia and ammonium chloride. The precipitates are filtered, washed, and ignited and weighed, heating, cooling in a desiccator and weighing carried out till the weights are constant.

It will be found, if the experiment be carefully performed, that the weights of magnesium pyrophosphate so obtained are the same, proving thereby that we are dealing with the same element.

(2) When red phosphorus is heated in an inert atmosphere above 550°C. so that vapours are produced and the vapours are rapidly cooled, yellow phosphorus is obtained. And if yellow phosphorus is heated to 240°C. in an inert atmosphere with a trace of iodine, red phosphorus is formed. The interconvertibility shows that yellow P and red P are allotropic modifications of the same element.

Phosphorus is chiefly used in the manufacture of matches. Large quantities of white phosphorus are converted into phosphorus trisulphide, P_2S_3, and red phosphorus, both of which are employed in the manufacture of matches. Formerly white phosphorus was used on match-heads, but this is now prohibited in most countries on account of its poisonous nature. In the present-day *safety matches*, the match-head consists of antimony trisulphide and lead dioxide or potassium chlorate and is ignited by rubbing against a specially-prepared surface on the match-box, which contains a mixture of red phosphorus, glue and an abrasive like broken glass.

Red phosphorus is used in the laboratory preparation of HBr and HI. White phosphorus is employed in the manufacture of P_2O_5, PCl_3 and PCl_5. Another use of phosphorus is in making phosphor bronze, an alloy of copper and tin containing 0·25 – 2·5% of phosphorus. Mixed with flour and grease, white phosphorus is used as a poison for rats and mice.

Phosphorus was used, during the World War I, in making incendiary bombs.

Q. 5. *Name the important ores of lead and give their formulae. How is lead extracted from its sulphide ore? State the uses of lead and its important alloys.*

Describe the action of water upon lead.

Ans. The important ores of lead are

Galena—PbS
Anglesite—$PbSO_4$
Cerrussite—$PbCO_3$

The extraction of lead from its sulphide ores consists of four operations :

1, **Concentration** : The ore is first of all concentrated by oil floatation process. The powdered ore is mixed with water, a little pine oil and the mixture churned by passing a current of air through it. By this operation, the sulphide ore of lead rises to the surface as scum, being wetted by oil and the gangue material sinks to the bottom, being wetted by water. The scum is collected and dried.

2. **Roasting and Sintering** :—The concentrated ore is then mixed with lime and taken in a vessel provided with a hood at the top for sucking away the fumes produced to a dust-collecting plant, and a grating at the bottom. A coal-fire is lighted by placing the coal on the grating and igniting the same, and an air-blast is put on. Lead sulphide is thereby converted into its oxide, sulphur dioxide escapes as gas and fumes evolved collect inside the dust-collecting chamber after passing through the hood. The powdery mass is converted into a hard coarse cake suitable for charging into the blast furnace. During roasting, sulphur present in the ore burns away forming sulphur dioxide :

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

Then, with increasing air-blast, the charge sinters together to a large cake. The cake is taken out and broken up into lumps suitable for charging into the blast furnace. Lime added to the charge serves the two-fold purpose of preventing fusion and of removing sulphur dioxide completely.

The sintered ore is next mixed with coke and a flux consisting of ferric oxide (raw iron ore) and lime and the mixture is charged into a water-jacketted blast furnace. A coal-fire is lighted at the bottom of the furnace and the charge is then introduced and in the meantime the air-blast is turned on through the tuyeres. The lead oxide present in the charge is reduced by carbon .

$$PbO + C = Pb + CO.$$

The carbon monoxide formed also helps in bringing about the reduction of lead oxide to a certain extent.

$$PbO + CO = Pb + CO_2.$$

Any unchanged lead sulphide also helps in bringing about the reduction of the lead oxide to metallic lead :

$$2PbO + PbS = 3Pb + SO_2.$$

Lime, added to the charge, combines with the silica present in the charge producing fusible calcium silicate. Iron oxide added to the charge helps to remove any lead sulphide remaining unacted upon, in the charge.

$$CaO + SiO_2 = CaSiO_3.$$

$$2PbS + Fe_2O_3 + 3C = 2FeS + 2Pb + 3CO.$$

Metallic lead produced collects in the molten condition at the bottom of the hearth and is tapped out therefrom by means of a tap-hole from time to time. The slag, consisting of calcium silicate and ferrous sulphide in the molten condition, is drawn off from time to time through the slag-hole.

Uses of lead :—

Lead is used (*i*) for making pipes, cisterns, bullets ; (*ii*) in storage battery ; (*iii*) in preparing alloys like type metal, solder and pewter ; (*iv*) in the construction of lead chambers for the manufacture of H_2SO_4, and (*v*) in preparing sheaths for electric cables. **Alloys of lead** are (1) Type metal—(Alloy of Pb, Sb, Sn) used for preparation of printing types.

(2) Soft solder— (Alloy of Pb + Sn)	used for soldering two pieces of metal or for stopping holes in metallic containers.
(3) Pewter— (Alloy of Pb + Sn)	used similarly as also for making table wares.

(4) Linotype metal, Ulco and Frary metal are other alloys of lead used for different purposes.

Action of water upon lead :—

Pure distilled water has practically no action upon lead in absence of air ; but water containing dissolved air dissolves the metal. Hydrated oxide of lead is first formed and a little H_2O_2 is found in solution. Lead hydroxide is appreciably soluble in water and so it passes into solution.

The solvent action of water on lead is determined by the presence of other substances held in solution in water ; thus—

(*a*) If water contains such substances in solution which give rise to soluble compounds of lead, then it will rapidly dissolve the metal. Thus, lead is readily attacked by water containing small amounts of nitrates, ammonium salts, etc.

(*b*) If, on the other hand, water contains in solution such substances which are capable of forming insoluble compounds of lead, then a coating of the insoluble compounds of lead is formed on the surface of the metal ; hence though such sample of water may slowly attack lead at first, the action will subsequently stop altogether. Thus, water containing phosphates, carbonates, sulphates in solution has practically no action on lead.

Q. 6. *Describe the manufacture of caustic soda and chlorine from common salt. State their uses.*

Explain, giving equations, what happens when a solution of caustic soda is

(*a*) *added to a solution of zinc sulphate ;*

(*b*) *heated with yellow phosphorus.*

Ans. Common salt (sodium chloride, NaCl) is dissolved in water and the solution of common salt (called brine) is subjected to electrolysis in a diaphragm cell, *e.g.*, Nelson cell. The separation of caustic soda formed at the cathode from the chlorine evolved at the anode is to be effected very efficiently, otherwise sodium chloride, hypochlorite, chlorate, etc. will be produced. The reactions that occur during the electrolysis are

$2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$ (in aqueous solution)
$2Na^+ + 2e = 2Na$ (at cathode)
$2Na + 2H_2O = 2NaOH + H_2$ (evolved as gas at cathode)
$2Cl^- - 2e = 2Cl$ (at anode)
$Cl + Cl = Cl_2$ (evolved as gas at anode),

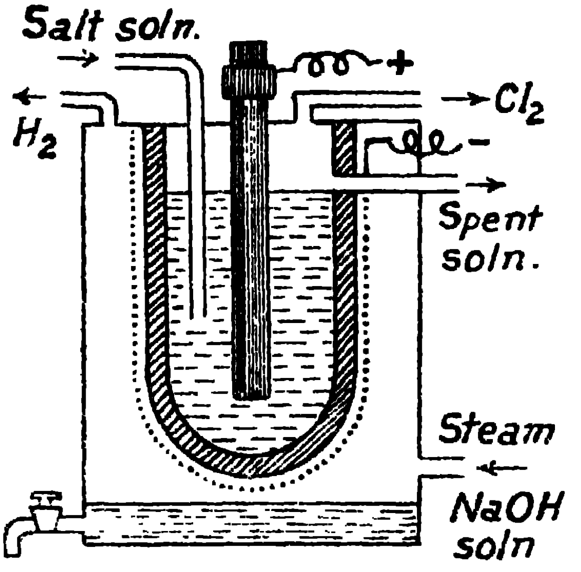


Fig. 43

In Nelson's cell a perforated steel cathode, made in the form of a long U-shaped trough, is suspended in a rectangular steel tank in which steam can be injected. The cathode is lined inside with asbestos. The anode is a carbon rod kept dipping into brine contained in the U-shaped steel trough. The asbestos lining of the cathode prevents the chlorine liberated from coming in contact with the caustic soda solution.. Brine is introduced through a pipe as required. Brine cannot pass throug the asbestos lining, but sodium ions pass through it and change to sodium atoms at the cathode. These sodium atoms next react with steam introduced by a side pipe in the tank to form caustic soda,

$$2Na + 2H_2O = 2NaOH + H_2.$$

Chlorine is led off from near the anode as shown in the figure. The caustic soda solution formed collects at the bottom of the steel tank and taken off from time to time by opening the tap set at the bottom of the tank. The solution of caustic soda is then evaporated in iron vessels. The solid so obtained is finally melted down and cast into sticks, pellets or balls.

Chlorine is evolved during this manufacture of caustic soda at the anode which is led off by an outlet pipe, and collected over brine. For industrial purpose it is dried by conc. H_2SO_4, liquefied and the liquid is stored in iron cylinders.

Uses of caustic soda :—Caustic soda is employed (1) in the preparation of soap, (2) in the manufacture of metallic sodium, (3) in the refining of petroleum, (4) in the manufacture of artificial silk, (5) in the textile, pulp and paper industries, (6) in reclaiming rubber and (7) in the laboratory as a reagent.

Uses of chlorine :—

Chlorine is used in the manufacture of bleaching powder, chloroform, bromine, chlorates, etc., as a disinfectant, for preparing pure HCl and for preparing certain poisonous gases like phosgene gas, mustard gas, etc., in the extraction of gold and for refining petroleum.

(*a*) When a solution of caustic soda is added gradually to zinc sulphate solution, at first a white precipitate of zinc hydroxide is formed, which dissolves on adding excess of caustic soda with the formation of sodium zincate, Na_2ZnO_2. Sodium sulphate is the other product.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

(*b*) When yellow phosphorus is heated with a solution of caustic soda, phosphoretted hydrogen or phosphine, PH_3, is evolved as a gas and sodium hypophosphite, NaH_2PO_2 is formed in solution.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Q. 7. *Describe experiments to demonstrate that :*

(*a*) *water is produced in many cases from a burning flame* ;

(*b*) *the simultaneous presence of air, water and carbon dioxide is necessary for the formation of rust on iron* ;

(*c*) *nitric acid contains oxygen* ;

(*d*) *caustic soda contains hydrogen* ;

(*e*) *the terms 'combustible' and 'supporter of combustion' are purely relative.*

Ans. (*a*) A flask containing cold water is placed on an wire gauze and a coal gas flame or flame produced by burning hydrocarbons is placed beneath the wire gauze. Droplets of water are found to collect on the outer surface of the cold flask. Water vapour that is first formed in the flame can be condensed to liquid water in contact with cold surface. Hence we conclude that in flames of coal gas or of hydrocarbons, water is produced as water vapour.

(*b*) A bright iron wire is cut into several pieces ; (*i*) one piece is placed in a porcelain basin kept inside a desiccator. In dry air present inside the desiccator, the piece of iron remains as bright as before even after several days. So no rusting takes place in dry air. (*ii*) Another piece is placed in a glass-stoppered bottle filled completely with air-free water. Here also iron shows no sign of rusting even after a long period of time. (*iii*) Another piece of iron wire is placed in another stoppered bottle containing a little quantity of water along with CO_2—free air (air after passing through KOH solution is admitted into the stoppered bottle.) Here also no rusting takes place. (*iv*) Then in another stoppered bottle a bright piece of iron wire is introduced along with a little quantity of water, air and carbon dioxide. The piece of iron wire is found to loose its brightness very soon and after a day or two brown specks of rust appear on the surface of the iron wire.

Thus we conclude that all three factors, water, air and carbon dioxide, are necessary for rusting of iron to take place.

(*c*) Conc. nitric acid is dropped slowly into a strongly heated clay tobacco pipe. Nitric acid breaks up by the heat into oxygen, nitrogen peroxide and steam. The gases are passed through water and collected in a gas jar by displacement of water. Nitrogen peroxide dissolves in water and steam condenses to water. Oxygen alone collects in the gas jar. That the gas is oxygen is proved by the facts that it rekindles a glowing splinter, produces brown fumes with nitric oxide and is completely absorbed by alkaline pyrogallate.

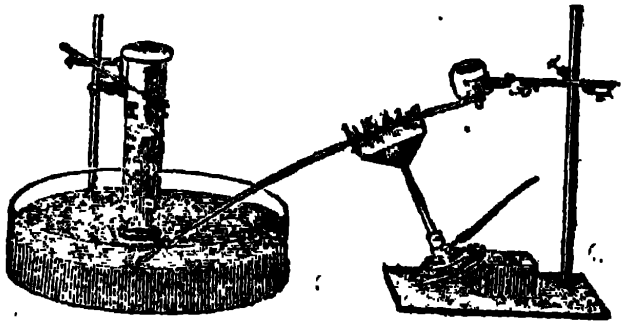


Fig. 44

(*d*) Fused caustic soda is heated strongly with metallic zinc. A gas is evolved and is collected by displacement of water in a gas-jar. That the gas is hydrogen is proved by the facts that (*i*) it burns with a scarcely visible blue flame with the production of water alone and no CO_2 as tested with lime water ; (*ii*) it forms an explosive mixture with O_2 and (*iii*) it is absorbed by heated palladium. These facts prove that caustic soda contains hydrogen, since it cannot come from zinc.

$$Zn + 2NaOH = Na_2ZnO_2 + H_2.$$

(*e*) Any chemical reaction accompanied by the evolution of heat and light is called *combustion*. Now it is customary to classify the substances taking part in combustion as the combustible bodies and supporters of combustion. Usually we call those substances which burn *combustible* and the atmosphere surrounding the burning substance, *supporter of combustion.*

Thus paraffin, hydrogen, carbon monoxide, etc., are combustible substances ; while oxygen, air, etc., are supporters of combustion.

This distinction, however, is a purely conventional one, and the two terms are purely relative. By a slight modification of the conditions, either H_2 or CH_4 or coal gas may become supporter of combustion and O_2 or Cl_2 the combustible body. This can be illustrated by the following experiment :—

A glass chimney is taken provided with a cork at its bottom. Two glass tubes, one short and the other long, are inserted through the cork at the bottom. A small sheet of asbestos with a hole at the middle is placed at the top of the chimney. Hydrogen is passed through the short tube till the chimney is completely filled up with hydrogen. Hydrogen is ignited as it comes out at the top through the hole in the asbestos. Now oxygen is passed in through the long tube and the gas is ignited by pushing the long tube up to the burning hydrogen. The long tube is then drawn into the middle of the chimney. We have got here two flames : one at the top of the chimney, where hydrogen burns in excess of air, and the other inside the chimney where oxygen burns in hydrogen. Similar experiment can be arranged with coal gas and oxygen or chlorine and hydrogen. Thus the supporter of combustion in one case can be made combustible in the other. Hence the terms are *relative.*

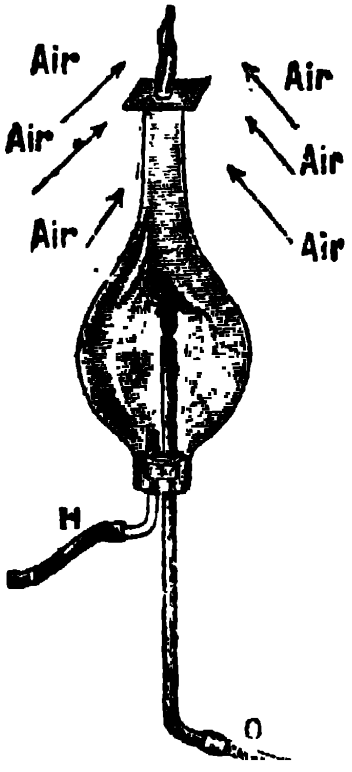


Fig. 45.

Q. 8. *Describe briefly the manufacture of sulphuric acid by contact process.*

Ans. A mixture of $SO_2 - 7\%$, $O_2 - 10{\cdot}4\%$ and $N_2 - 82{\cdot}6\%$ is obtained by burning iron pyrites, FeS_2, in kilns with the requisite supply of air. The gas mixture is carefully purified by passing (1) through a dust chamber in which steam is injected ;

(2) then through a series of lead pipes to reduce the temperature of the gas mixture down to 100°C. ; (3) through a series of towers in which it meets a descending spray of water which washes the H_2SO_4 formed in the kiln gases ; and finally (4) the gas mixture is dried by passing them up through a tower where it meets the descending stream of strong H_2SO_4. The gas mixture is then examined by a powerful beam of light in the testing chamber. The absence of fog indicates that the gas mixture has been sufficiently purified. It is then led into the contact chamber. It consists of an iron cylinder inside which are several iron pipes loosely packed with platinised asbestos between perforated shelves. This platinised asbestos serves as the catalytic agent. The mixture of SO_2 and air enters the chamber at the bottom, passes upto the top of the cylinder around the outside of these tubes and then descends through the inside of these tubes, passing over the catalyst packed therein. The contact chamber is heated to 400°–450°. by ring burners placed at the bottom to start the reaction. Considerable heat is evolved during the oxidation of SO_2 to SO_3 according to the reaction $2SO_2 + O_2 = 2SO_3$ and the tubes have a tendency to get hotter during the reaction. Heat-interchange takes place between the cold gases sweeping over the outside of the tubes and the hot gases inside the tube, and temperature is maintained constant at about 450°C.

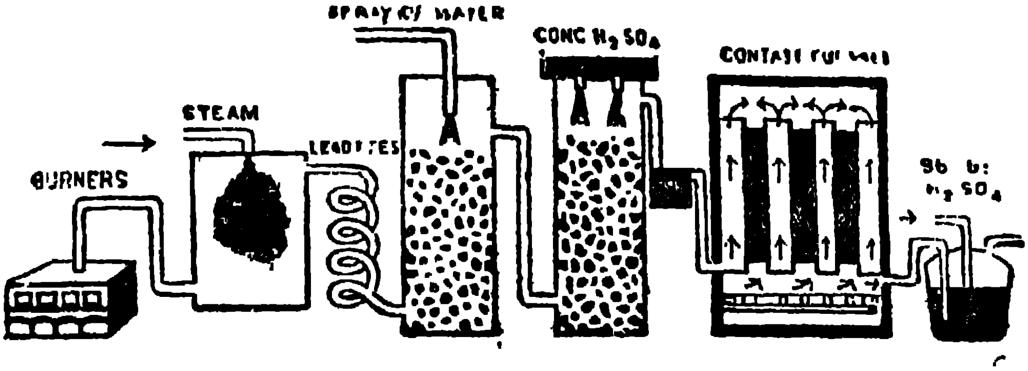


Fig. 46

No further external heating is necessary and the reaction goes on automatically.

The issuing gas is cooled and then passed through 98% sulphuric acid in iron towers. SO_3 is absorbed. A stream of water or dilute H_2SO_4 is run in at such a rate that the concentration of the acid is maintained at 97—98 per cent.

$$H_2SO_4 + SO_3 = H_2S_2O_7$$
$$H_2S_2O_7 + H_2O = 2H_2SO_4.$$

SECOND PAPER—1947

Q. 1. *What is meant by the equivalent weight of an element? Illustrate your answer with examples.*

0·33 grams. of a metal on dissolving in dilute sulphuric acid, liberates 113 c. c. of dry hydrogen at N. T. P. Determine the equivalent weight of the metal.

Ans. The equivalent weight of an element is that weight of it which combines with or displaces from a compound one part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine. It is a mere number, since it can be expressed as

$$\textit{Chemical equivalent} = \frac{\text{wt. of the element in certain unit}}{\text{wt. of hydrogen displaced by or combined with the given wt. of the element in the same unit.}}$$

Thus, 12 parts by wt. of Magnesium can displace 1 part by weight of hydrogen.

Hence 12 is the chemical equivalent of Mg.

Also 23 parts by wt. of Na can displace 1 part by weight of hydrogen. Hence 23 is the equivalent weight of sodium.

Again 31·75 parts by weight of copper combine with 8 parts by weight of oxygen. Hence 31·75 is the equivalent weight of copper.

Also 20 parts by weight of calcium combine with 35·5 parts by weight of chlorine. Therefore 20 is the equivalent weight of calcium.

Wt. of 113 c.c. of *dry* hyrogen at N.T.P. $= 113 \times 0·00009$ gra $= 0·01017$ gram.

Equivalent weight of the metal

$$= \frac{\text{wt. of the metal taken}}{\text{wt. of hydrogen liberated by it}} = \frac{0{\cdot}33 \text{ gram.}}{0{\cdot}01017 \text{ gram}} = 32{\cdot}4.$$

Q. 2. *Describe the Kipp's apparatus.*

Make a clean sketch of this apparatus showing its use for the preparation of dry carbon dioxide. What happens when a burning magnesium ribbon is introduced into a jar of carbon dioxide?

Ans. Kipp's apparatus, as shown in the adjoining figure, consists of two separable parts. The upper part consists of a glass globe with a long stem ; the lower portion consists of two glass globes joined at the middle by a short neck. The lowest globe is flattened at the bottom, so that during use, after fitting the whole apparatus, this can stand upon this flat bottom. The upper glass globe with the long stem serves as a big funnel. The upper glass globe with the long stem fits air-tight into the neck of the central globe, the stem reaching nearly to the bottom of the lowest globe. A glass stop-cock is fitted through a rubber cork to the middle glass globe as shown in the figure. The lowest globe is provided with an outlet kept closed by means of a ground glass stopper, so that the waste liquid may be drawn off from the bottom. There is often a bent funnel fitted through a rubber cork to the uppermost globe for pouring in liquid necessary for the preparation of any gas. The apparatus is used for preparing gases which require no heating and continuous supply being required, *e.g.*, H_2S, CO_2, H_2.

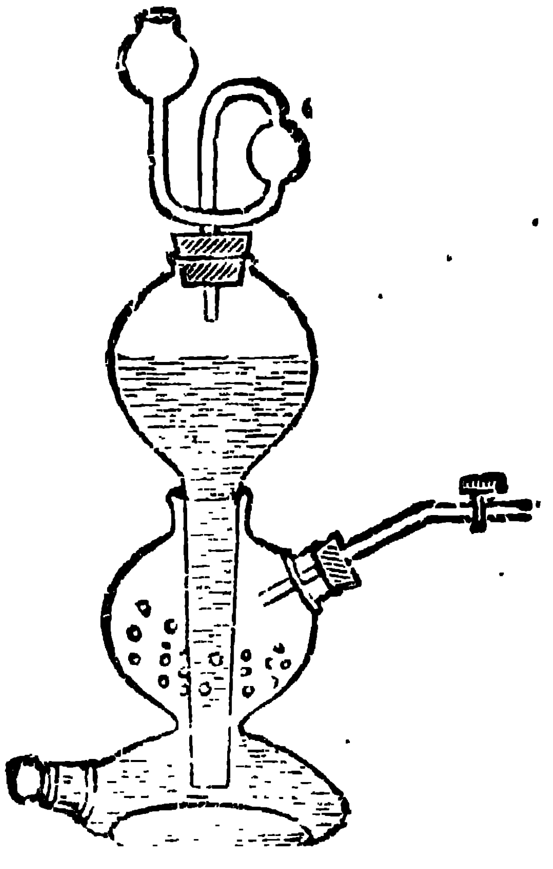


Fig. 47.

For the preparation of dry carbon dioxide with it, the Kipp's apparatus is to be attached through the delivery tube to a wash-bottle containing concentrated H_2SO_4 for drying the gas. Chips of marble are placed in the middle globe and dilute hydrochloric acid is poured through a thistle funnel fitted to the neck of the upper globe. Thus the lowest globe and half of the middle globe containing marble chips are filled with the acid, which reacts with the marble chips and carbon dioxide escapes through the side delivery tube and then passes through the washer containing conc. H_2SO_4 by which it is dried. When the gas is not required the stop-cock is closed, and the gas, being unable to escape, exerts pressure on the liquid surface and displaces the acid from the central globe to the upper one. The acid being no more in contact with marble chips, reaction stops. On reopening the stop-cock, the gas escapes ; the pressure is thus released, the acid rises again in the middle globe and reacts with the marble chips and carbon dioxide is evolved.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

When a burning magnesium ribbon is introduced into a jar of carbon dioxide, it continues to burn and soot is deposited inside the jar, due to separation of carbon from carbon dioxide and a white deposit of magnesium oxide is formed in the jar.

$$2Mg + CO_2 = 2MgO + C.$$

Q. 3. *How will you prove that air is a mechanical mixture ?*

What experiments will you perform to show that one of the main constituents of air is present in each of the following substances : (a) ammonia, (b) red lead, (c) marble and (d) crystals of copper sulphate ?

Ans. The following are the reasons for considering air to be a mechanical mixture of nitrogen and oxygen :—

(1) In a mechanical mixture of two or more substances the properties of the different ingredients are retained, but when a compound is formed from two or more ingredients, the molecules of the ingredients are changed and new molecules are formed. These new molecules have properties altogether different from those of the ingredients.

Now, we can infer air to be a mechanical mixture of nitrogen and oxygen, because the properties of both nitrogen and oxgen are found to be present in air, for example, oxygen is a supporter of combustion, so is also air, though to a less extent on account of its dilution. Oxygen is absorbed by alkaline pyrogallate, and alkaline pyrogallate can absorb and remove oxygen from air. After removal of oxygen from air by absorption with alkaline pyrogallate, nitrogen left shows all the properties of nitrogen.

Therfore air is considered to be a mechanical mixture.

(2) The analyses of samples of air drawn from different localities and different altitudes show that the proportion of nitrogen and oxygen in air by weight is *nearly* constant, yet slight variations are noticeable. But even the slightest deviation from fixed composition is not possible in the case of a chemical compound.

Air is thus proved to be a mixture of oxygen and nitrogen.

(3) When gases combine chemically there is always a thermal change, and oftentimes a change in volume is observed. But when 23 parts by weight of oxygen are mixed with 77 parts by weight of nitrogen, there is neither any heat change nor any change in volume. Yet the mixture behaves in every respect like ordinary air.

Thus, air is a mechanical mixture.

(4) The density and other physical properties of air are average of these properties of the constituents nitrogen and oxygen, in the proportion in which they are present in air. Thus, taking d to be the density of air which contains nitrogen and oxygen in the proportion 4 : 1 by volume approximately, we can calculate d as follows :—

Wt. of air = Wt. of nitrogen + Wt. of oxygen.

Taking into consideration 100 volumes of air consisting of 80 volumes of nitrogen and 20 volumes of oxygen,

$$\begin{aligned} 100 \times d &= 80 \times 14 + 20 \times 16 \\ &= 1120 + 320 \\ &= 1440. \\ \therefore\quad d &= 14{\cdot}4. \end{aligned}$$

The observed density of air is also 14·4, just the value calculated on the assumption that air is a mechanical mixture.

Therefore air is nothing but a mechanical mixture.

(5) There are five different oxides of nitrogen whose gravimetric compositions are such that they obey the *Law of Multiple proportions.* The composition of air by weight

(77 nitrogen, 23 oxygen) is such that no simple formula can be assigned to it (77 parts by weight of nitrogen stands for 5½ atoms of nitrogen and 23 parts by weight of oxygen stands for 1·4375 atoms of oxygen). Thus the Law of Multiple proportions as applied to the case of definite oxides of nitrogen cannot be applied here. Also if a tentative formula for air (considering it to be a compound) is found out, the density of air calculated on that basis comes out to be much higher than its actual density.

Therefore air is a mechanical mixture.

(6) The ingredients of a mechanical mixture can be separated by easy mechanical means of separation like diffusion, distillation, vaporisation, etc., but the components of a chemical compound can not be so separated.

The constituents of air can be separated (*a*) *by diffusion* : When air is passed through a porous tube, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen and the residue left is found to be richer in oxygen than ordinary air. Had air been a chemical compound, no such separation of the constituents would have been possible.

(*b*) *by vaporisation* : When liquid air is allowed to evaporate, the boiling point increases progressively. Further, the gas which comes out first is richer in nitrogen than the gas which comes out afterwards. Thus liquid air is to be considered as a mixture of two liquids, liquid nitrogen and liquid oxygen, and it may be presumed that atmospheric air is also a mixture of the gases, nitrogen and oxygen.

(*c*) *by solution in water* : If air be shaken with water, a part of it goes into solution and the dissolved gas can be expelled by boiling, It has been found that the air thus recovered from solution is very much richer in oxygen than ordinary air. Thus a partial separation of the ingredients of air by solution in water followed by subsequent heating, *i.e.*, by easy mechanical means is possible.

Air is thus a mechanical mixture. Any single argument given in the above discussion may not be considered sufficient, but the arguments taken all together prove completely that air is a mechanical mixture, and *not a compound*, of nitrogen and oxygen.

(*a*) Ammonia in solution in water is treated with chlorine gas when a gas is evolved which can be collected by displacement of water. That the gas is nitrogen can be proved by the facts that it is inert, it does not support combustion and is absorbed by heated magnesium without separation of soot. But nitrogen is also known (from experiments carried out by burning P in a closed volume of air and dissolving out the P_2O_5 formed with water) to be one of the main constituents of air. Thus ammonia is proved to contain one of the main constituents of air, *viz.*, nitrogen.

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

(*b*) Red lead is taken in a hard glass test tube and heated strongly above 450°C., when a gas is evolved, which can be collected by displacement of water. That the gas is oxygen can be proved from the facts that it supports combustion very vigorously and is absorbed completely by alkaline pyrogallate. Now the fact that air contains oxygen has been proved by heating Hg for a time in contact with a closed volume of air and then after cooling red scales floating on mercury are collected: these red scales on heating provides oxygen (tested as before). Also oxygen in air can be dissolved out by alkaline pyrogallate. Thus it is proved that red lead contains one of the main constituents of air, *viz.*, oxygen.

$$2Pb_3O_4 = 6PbO + O_2.$$

(*c*) When marble is heated, a gas is evolved which turns lime-water milky and which extinguishes a lighted taper just like water. So the gas is proved to be carbon dioxide. Carbon dioxide is also one of the main constituents of air, as is proved by blowing air through lime-water which turns milky or by the appearance of a scum on the surface of lime-water kept exposed to air in a saucer. Thus, marble contains one of the main constituents of air, *viz.*, carbon dioxide.

$$CaCO_3 = CaO + CO_2.$$

(*d*) Crystals of copper sulphate, when heated, evolve water vapour which can be condensed to liquid state by cooling and collected as such. That the liquid is water can be proved by adding anhydrous copper sulphate, which is white, to it when it will turn blue. Presence of water vapour in air is proved by placing a lump of ice in a beaker containing water, when the outside surface of the beaker will be covered with minute drops of water formed by the condensation of water vapour present in air, in contact with the cold surface. The same fact is proved by the deliquescence of fused $CaCl_2$. Thus, crystals of copper sulphate contain one of the main constituents of air, *viz.*, water.

Q. 4. *Some iodine got mixed up with potassium iodide. How will you separate them ?*

Discuss the chemical changes that take place when

(a) iodine is mixed with caustic soda solution,

(b) potassium iodide is mixed with concentrated sulphuric acid,

(c) gaseous chlorine is passed into aqueous solution of potassium iodide and

(d) potassium iodide solution is added to mercuric chloride solution.

Ans. In order to separate iodine from potassium iodide, the mixture is heated in a basin covered over with a clock glass over which a moist piece of filter paper is placed. Iodine sublimes off and collects on the lower surface of the clock glass.

(*a*) When iodine is mixed with cold and dilute caustic soda solution, sodium iodide and sodium hypo-iodite, which is subsequently hydrolysed to hypoiodous acid, are formed.

$$2NaOH + I_2 = NaI + NaOI + H_2O$$
$$NaOI + H_2O \rightleftharpoons HOI + NaOH,$$

Iodine, on being mixed with hot and concentrated caustic soda solution gives sodium iodide and sodium iodate.

$$6NaOH + 3I_2 = NaIO_3 + 5NaI + 3H_2O.$$

(*b*) When potassium iodide is mixed with concentrated H_2SO_4, HI is first evolved, but the mixture soon gets heated and violet vapours of iodine are evolved.

$$2KI + H_2SO_4 = K_2SO_4 + 2HI$$
$$2HI + H_2SO_4 = I_2 + 2H_2O + SO_2.$$

(*c*) When gaseous chlorine is passed into aqueous solution of potassium iodide, at first iodine is liberated and the solution turns brown. But with continued passage of chlorine gas the solution turns colourless due to the formation of iodic acid by the oxidation of iodine carried out by chlorine.

$$2KI + Cl_2 = 2KCl + I_2$$
$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

(*d*) When potassium iodide solution is added to mercuric chloride solution, at first a red precipitate of mercuric iodide is produced. On addition of excess of potassium iodide solution the red ppt. of mercuric iodide dissolves forming potassium mercuri-iodide.

$$2KI + HgCl_2 = HgI_2 + 2KCl$$
$$2KI + HgI_2 = K_2HgI_4.$$

Q. 5. *How is sodium prepared? Give a neat sketch of the apparatus used for this preparation.*

Discuss the action of this metal on : (a) dry oxygen, (b) hydrogen chloride, (c) mercury and (d) water.

Give equations to represent the reaction.

Ans. Sodium is prepared from caustic soda, NaOH, by Castner's process. Fused caustic soda is electrolysed in a cylindrical iron vessel which is provided with a narrow cylindrical base as shown in the adjoining figure. An iron cathode is introduced through the narrow cylindrical bottom and is kept in position by the solidified caustic soda present therein. The anode is made of nickel and is cylindrical and hollow, placed in such a

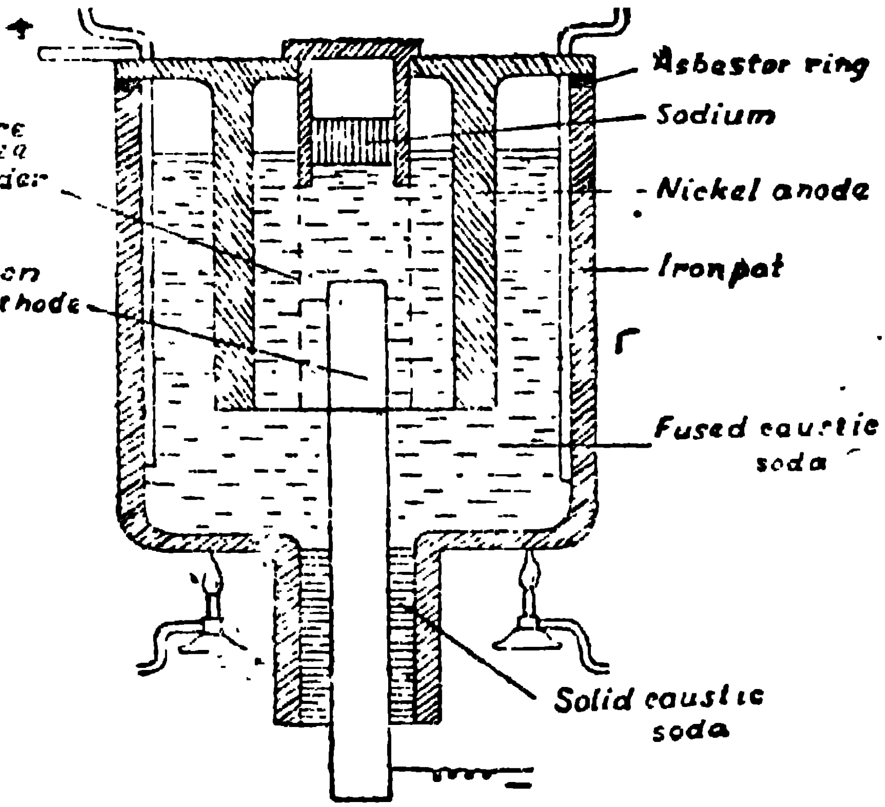


Fig. 48

way suspended from the top of the iron vessel that it surrounds the upper part of the iron cathode.

Caustic soda is melted down and kept in molten condition by a set of ring burners placed at the bottom. On passing the electric current through this molten NaOH it decomposes into sodium, oxygen and hydrogen. Sodium and hydrogen comes out at the cathode while oxygen is liberated at the anode. Sodium, being lighter than fused caustic soda, floats on the fused NaOH and collects in a metal cylinder provided with a loose cap at the top to allow the hydrogen to escape from time to time ; there is also a wire gauze netting at the bottom of this metal cylinder as shown in the figure by the dotted lines. The atmosphere of hydrogen in the metal cylinder prevents sodium from undergoing oxidation by atmospheric oxygen. Sodium is removed from time to time by means of perforated ladle, which retains metallic sodium, allowing the fused caustic soda to flow down to the bath.

$$NaOH \rightleftharpoons Na^{+} + OH^{-}$$
$$OH^{-} \rightleftharpoons H^{+} + O^{--}$$
$$\left.\begin{array}{l} Na + \underset{\text{(electron)}}{e} \rightarrow Na \\ 2H^{+} + 2e \rightarrow H_2 \end{array}\right. \quad \text{at the cathode}$$
$$2O^{--} - 4e \rightarrow O_2, \text{ at the anode.}$$

(*a*) Sodium reacts with ordinary dry oxygen, when heated giving sodium monoxide (at 180°C.) and sodium peroxide (at 300°).

$$4Na + O_2 = 2Na_2O$$
$$2Na + O_2 = Na_2O_2.$$

Perfectly dry oxygen is without action upon sodium.

(*b*) Sodium reacts with hydrogen chloride at ordinary temperature, forming sodium chloride and evolving hydrogen gas.

$$2Na + 2HCl = 2NaCl + H_2.$$

(*c*) Sodium reacts with mercury forming sodium amalgam.

$$Na + Hg = NaHg.$$

(*d*) Sodium reacts with water even in the cold evolving hydrogen gas and forming sodium hydroxide.

$$2Na + 2H_2O = 2NaOH + H_2.$$

Q. 6. *Write an account of the extraction of aluminium from its ore.*

What are the important alloys of this metal and how are they prepared? Mention the uses of the metal and its alloys.

Ans. Aluminium is extracted from its ore, *bauxite*, Al_2O_3, $2H_2O$. Naturally occurring bauxite is impure ; it contains iron oxide and silica. So it is to be purified before it can be utilised for the extraction of aluminium. Thus the extraction of aluminium from bauxite consists of two operations, *viz.*, purification of bauxite and electrolysis of fused bauxite in a bath of molten cryolite.

Purification of bauxite : Powdered bauxite is fused with sodium carbonate in a furnace, whereby sodium aluminate is formed along with a little sodium silicate, iron oxide being left as such.

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2.$$

The fused mass is cooled and rapidly lixiviated with water when sodium aluminate passes into solution, leaving iron oxide behind. The solution of sodium aluminate is next heated to 50°—60°C. and CO_2 is passed into it, when hydrated aluminium oxide is precipitated :

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3.$$

The hydrated aluminium oxide is filtered, washed, dried and ignited.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

Modern Baeyer's process consists in calcining the natural bauxite and then digesting the calcined bauxite with strong caustic soda solution at a pressure of 80 lbs. and at a temperature of 150°C. Sodium aluminate is formed in solution and iron oxide, iron hydroxide etc. remain as insoluble matter.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O.$$

The solution is cooled, diluted and filtered. The filtrate is then treated with some freshly precipitated $Al(OH)_3$ obtained in the previous batch and vigorously agitated when most of the aluminium present in solution is precipitated as aluminium hydroxide.

$$NaAlO_2 + 2H_2O = NaOH + Al(OH)_3.$$

The precipitated aluminium hydroxide is filtered, washed, dried and ignited, when pure alumina is obtained.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

Extraction of Aluminium from purified bauxite by electrolysis :—

Purified bauxite is next dissolved in a bath of molten cryolite, and electrolysed in an electric furnace. The furnace consists of a rectangular iron box lined inside with blocks of gas carbon. This iron box is made the *cathode*. The anode consists of 3 or 4 stout carbon rods attached to a rod of copper and suspended in the molten bath. A little fluorspar is added to the bath in order to increase its fluidity. When electric current is passed in, alumina undergoes decomposition. Aluminium, liberated at the cathode, sinks in the liquid state to the bottom whence it is taken out by means of the tap hole. Oxygen, liberated at the anode, attacks the carbon rods producing CO and CO_2 which are given off.

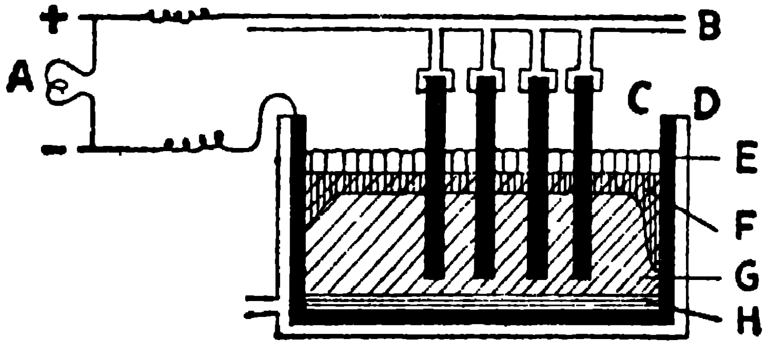


Fig 49

$$2Al_2O_3 = 4Al + 3O_2$$
$$C + O_2 = CO_2 ;$$
$$2C + O_2 = 2CO.$$

The resistance of the electrolyte gives sufficient heat to keep the mass in the fused condition. The temperature of the bath is usually maintained at about 950°C.

The method is continuous. When Al_2O_3 is used up, the resistance of the bath increases and then a lamp, which is shunted off the circuit, begins to glow. Fresh Al_2O_3 is then added and the electrolysis goes on and aluminium formed is tapped off from the bottom from time to time.

Important alloys of aluminium are

(1) Aluminium, bronze, an alloy of Al and Cu.
(2) Magnalium, an alloy of Al and Mg.
(3) Duralumin, an alloy of Al, Cu, Mg and Mn.

These alloys can be prepared by melting down Al admixed with the other metal or metals, in the right proportion, in an inert atmosphere like that of carbon dioxide or in a reducing atmosphere with the addition of a flux.

Uses of aluminium.—For the extreme lightness of the metal it is largely used for making air-ships and engine-parts. It is also used in the manufacture of utensils, surgical intruments, electric wires and cables (used in U.S.A.). It is used as a reducing agent in the production of Cr, Si, Mn, etc., by Goldschmidt's thermit process, in the manufacture of steel, for making light alloys like magnalium, duralumin, aluminium bronze, etc. It is also added to molten steel during casting in order to prevent formation of blow-holes. Al-powder is used as a paint for preserving iron articles against rusting as also in fire-works.

Of the alloys of aluminium mentioned, *aluminium bronze* is used for making cooking utensils, photo frames and other ornamental work ; *magnalium* is used for making cheap balances and other articles ; *duralumin* covered with a thin coating of pure aluminium is now used under the trade name of "alclad" in the construction of seaplanes.

Q. 7. *What happens when, (a) streams of ammonia and carbon dioxide gases are passed into a saturated solution of sodium chloride, (b) powdered slaked lime is mixed well with chlorine gas, (c) hydrated calcium sulphate is dried at 120°—130°C. and the powder so obtained is made into a paste with water, (d) into a mixture of ferric oxide and aluminium powder is thrust a piece of magnesium ribbon, which is subsequently lighted ?*

Represent the reactions involved by equations, as far as you can.

Ans. (*a*) Sodium bicarbonate is precipitated and ammonium chloride is formed in solution,

$$NaCl + H_2O + CO_2 + NH_3 = NaHCO_3 + NH_4Cl.$$

(*b*) Powdered slaked lime takes up chlorine with the formation of bleaching powder (calcium chloro-hypochlorite).

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

(*c*) Hydrated calcium sulphate ($CaSO_4, 2H_2O$) is converted at 120°—130°C. into Plaster of Paris, $2CaSO_4, H_2O$.

$$2(CaSO_4, 2H_2O) = (CaSO_4)_2, H_2O + 3H_2O.$$

The powder of Plaster of Paris, when made into a paste with water forms a hard mass on keeping. This is known as *setting* of Plaster of Paris. It is due to *rehydration* and re-conversion into hydrated calcium sulphate ($CaSO_4, 2H_2O$, gypsum).

$$(CaSO_4)_2, H_2O + 3H_2O = 2(CaSO_4, 2H_2O).$$

(*d*) The mixture of ferric oxide and aluminium power is known as *Thermit.* When the mixture is set fire to, by means of magnesium ribbon being lighted, aluminium liberates iron from ferric oxide, and the iron so liberated melts due to excessive heat developed in the reaction.

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

Q. 8. *How would you recognise whether a sample of water was hard or soft ? How can the hardness of water be removed ? Indicate how you would purify a sample of water* (*a*) *for drinking purposes,* (*b*) *for industrial purposes.*

Ans. Hardness of water can be detected (1) by use of soap. Hard water will not easily form lather with soap, but much soap will be wasted before any lather appears with hard water. (2) By boiling the water or by adding lime, when in case of temporarily hard water a granular precipitate will be formed. (3) By adding Na_2CO_3 when permanently hard water will give a precipitate.

Removal of hardness :—

(*a*) Temporary hardness can be removed *by boiling* when the soluble bi-carbonate of calcium and magnesium are converted into insoluble calcium or magnesium carbonates. On keeping, these settle down at the bottom of the vessel in which the water is boiled and the sample of water taken off from the top is soft.

$$\underset{\text{(Sol.)}}{CaH_2(CO_3)_2} = \underset{\text{(insol.)}}{CaCO_3} + H_2O + CO_2$$

$$\underset{\text{(Sol.)}}{MgH_2(CO_3)_2} = \underset{\text{(insol.)}}{MgCO_3} + H_2O + CO_2$$

Temporary hardness can also be removed by Clark's process.

In this process the requisite amount of lime in the form of lime-water or milk of lime is added to the temporarily hard water when soluble bicarbonate of Ca and Mg are converted into insoluble carbonates.

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

In the case of the hardness being due to magnesium bicarbonate, twice the quantity of lime must be added, since magnesium carbonate is soluble in water to a certain extent, whilst the hydroxide of magnesium is much less soluble.

$$MgH_2(CO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O.$$

Permanent hardness cannot be removed either by boiling or by Clark's process. This kind of hardness is removed by the addition of sodium carbonate (washing soda) when the soluble sulphates and chlorides of Ca and Mg present in permanently hard water are converted into the insoluble carbonates of Ca and Mg.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$
$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4.$$

The modern Permutit Process.—The most modern method for the removal of hardness, both temporary and permanent. is known as Gan's Permutit Process.

In this process bodies, called permutits, which are mixtures of aluminium silicate, sodium silicate (sodium alumino-silicate), etc. are employed. These silicate mixtures are called permutits because these have the capacity of exchanging bases.

The method depends upon the fact that if hard water is filtered through a bed of permutit, the sodium salt present in it will react with soluble calcium and magnesium salts present in hard water, producing insoluble calcium and magnesium permutits and the filtrate, being altogether free from Ca and Mg salts, is soft.

Sodium permutit + $CaCl_2 \rightarrow$ Ca-permutit + NaCl. When the permutit bed, due to long use, is exhausted, it is re-activated by stopping the flow of hard water and passing a solution of common salt, NaCl, over the bed when Na-permutit is regenerated according to the reaction.

$$\text{Ca-permutit} + NaCl \rightarrow \text{Na-permutit} + CaCl_2$$
$$\text{Mg-permutit} + NaCl \rightarrow \text{Na-permutit} + MgCl_2.$$

Thus permutit can be regenerated and used over and over again.

Purification of a sample of water for drinking purposes :—

At first a little alum is added and the suspended matter present in water is allowed to settle down. The clear water is then removed by decantation and finer particles of insoluble matter are removed by filtration through beds of sand, charcoal and gravel one after another. The clear water thus obtained is next sterilised by boiling (on a small scale) or by adding bleaching powder, or liquid chlorine, or by passing ozonised air through it, or by exposing it to ultraviolet rays from a mercury vapour lamp (on a large scale when pure drinking water is to be supplied to a town).

Purification of water for industrial purposes :—

Water to be used as boiler-feed water should be softened with care by adding lime and sodium carbonate and filtering off the ppt. formed. Water is often treated with sodium phosphate before adding to boilers in order to prevent formation of hard boiler-scales. Water to be used for medicinal preparations and in photography is to be very pure and hence it is to be obtained by distilling ordinary water. For medicinal preparations and injectules twice or thrice distilled water is often required.

FIRST PAPER—1948

Q. 1. *Explain and illustrate what you understand by the* **normality** *of an acid or base.*

What is meant by **neutralization ?** *25 c. c.'s of a solution of sulphuric acid neutralises 22·5 c. c,'s of a 4% solution of sodium carbonate. How would you reduce the strength of the acid to* **decinormal ?**

[Na = 23, S = 32]

Ans. Normality of the solution of an acid or base depends upon the multiple or submultiple of gram-equivalent of an acid or base being present in solution in 1000 c.c. of the solution of acid or base. By gram-equivalent of an acid we mean that weight (in grams) of it, which contains 1 gram of replaceable hydrogen. By gram-equivalent of a base we mean that weight of it (in grams) which will just completely neutralise one gram-equivalent of an acid. The normal solution is usually indicated by (N) solution. Thus 2(N) solution of an acid or base is that which contains 2 gram-equivalents of an acid or base dissolved in 1000 c.c. of the solution ; and $\frac{N}{5}$ solution is that which contains $\frac{1}{5}$th of the gram-equivalent of an acid or base in 1000 c. c. of the solution.

By *neutralization* we mean the reaction between an acid and a base in solution when the two are brought in contact with each other with the production of water and salt only.

In the light of the ionic theory, neutralization is the process of combination of H^+ – ions of an acid with the $(OH)^-$ – ions of an alkali forming undissociated molecules of water.

$$H^+ + OH^- = H_2O.$$

Sum.

4% solution of sodium carbonate

$\equiv$ 4 grams of sodium carbonate in 100 c. c. of the solution.

∴ Strength of sodium carbonate

$\equiv \frac{40}{53}$N, since 53 is the equivalent weight of sodium carbonate.

Let S be the strength of sulphuric acid.

Then since, $V \times S = V_1 \times S_1$, where

V = vol. of sulphuric acid

S = strength of „ „

V_1 = vol. of sodium carbonate

and S_1 = strength of sodium carbonate

$$\therefore \quad 25 \times S = 22{\cdot}5 \times \frac{40}{53}N$$

$$\therefore \quad S = \frac{22{\cdot}5}{25} \times \frac{40}{53}(N)$$

$$= 0{\cdot}679(N)$$

$$= 6{\cdot}79\left(\frac{N}{10}\right).$$

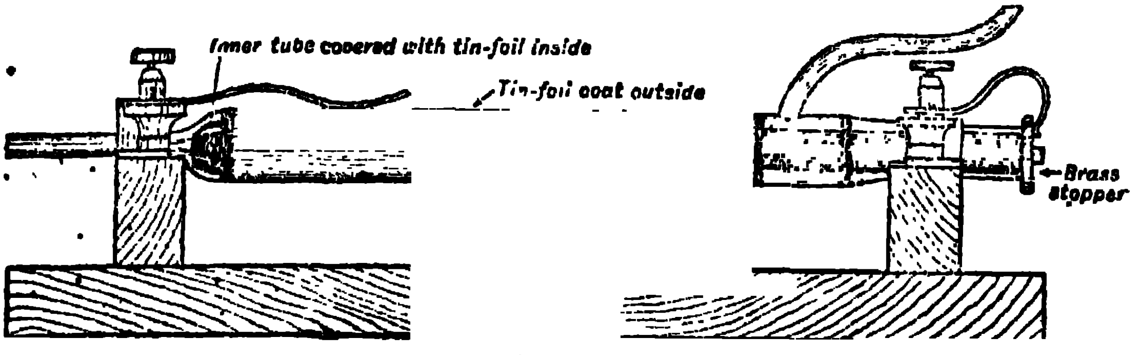
Thus 6·79 being the factor here of $\frac{N}{10}$ solution, 1 c. c. of the solution $\equiv$ 6·79 c. c. of $\frac{N}{10}$ solution.

Hence every 1 c. c. of the solution is to be diluted with 5·79 c. c. of water to give an exactly decinormal solution.

Q. 2. *How is ozone prepared in the laboratory? Describe its properties. How would you prove that ozone is condensed oxygen and its molecular composition is O_3? Describe any reaction by which you can distinguish between ozone and oxygen.*

Ans.

Laboratory preparation.—Ozone is best obtained by exposing pure dry oxygen to the action of silent electric discharge in Siemens' ozoniser which consists of two concentric glass tubes. The outer tube is coated outside and the inner lined inside with tinfoils. These tinfoils are connected with two binding screws which in their turn are in connection with a Ruhmkorff's coil. Dry oxygen is passed through the annular space in slow stream and a series of silent electric discharge is passed. The gas coming out at the exit consists of a mixture of oxygen and ozone. $3O_2 = 2O_3$.



Siemens' ozoniser.

Fig. 50.

The yield of ozone is only 5 to 8%.

Properties. *Physical.*—It is a pale blue gas with a fishy odour. It is slightly soluble in water, but readily dissolves in essential oils like oil of cinnamon or oil of turpentine. It is unstable and decomposes when heated to about 250°—300°C., being reconverted into oxygen.

Chemical.—It is a powerful oxidising agent. It oxidises S, P and As to their highest oxyacids.

$$S + H_2O + 3O_3 = H_2SO_4 + 3O_2.$$

It liberates halogens from their hydracids :

$$2HCl + O_3 = Cl_2 + H_2O + O_2.$$

It also liberates iodine from neutral potassium iodide :

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2.$$

It oxidises moist I_2 to HIO_3 :

$$I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2.$$

Lead sulphide is oxidised by ozone readily to lead sulphate, the colour changing thereby from black to white ;

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

In all these oxidation reactions, an equivalent amount of oxygen is set free. But in the oxidation of SO_2 to SO_3 and of $SnCl_2$ in HCl solution to $SnCl_4$, ozone is completely absorbed :

$$3SO_2 + O_3 = 3SO_3.$$
$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O.$$

Ozone oxidises mercury to Hg_2O ; a drop of mercury exposed to ozone loses its mobility and sticks to glass. It bleaches vegetable colours by oxidation. Ozone is catalytically decomposed by oxides of silver, iron, cobalt, etc. and by shaking it with powdered glass. Even metallic Ag, Pt and Pd decompose ozone catalytically.

That ozone is nothing but condensed oxygen is proved by the fact that when pure and dry oxygen enclosed over concentrated sulphuric acid in a graduated vessel is subjected to silent electric discharge, it is converted to ozonised oxygen with contraction in volume as indicated by the movement of the sulphuric acid level. This is also demonstrated in Newth's apparatus for determining the volumetric composition of ozone.

The apparatus consists of two concentric glass tubes, the inner tube fitted into the outer tube by a ground glass joint. The inner tube, which is nothing but an elongated hollow stopper, contains dilute H_2SO_4. The apparatus, previously filled with dry oxygen, is placed in a jar of water and crushed ice. Two platinum wires are dipped into the two liquids, one in dilute H_2SO_4 in the hollow stopper, and the other in the jar containing iced water and are connected with the terminals of an induction coil. A little oil of turpentine is contained in a little sealed thin glass tube, almost capillary in bore, which is held in position between four little projecting glass points upon the hollow stopper and the outer tube, as shown in the figure. A manometer, containing concentrated sulphuric acid coloured with indigo, is in communication with the apparatus. The levels of concentrated H_2SO_4 in the manometer are adjusted, and the oxygen is ozonised by passing electric discharge. A contraction in volume results. When sufficient contraction has taken place, the discharge is interrupted, the apparatus is allowed to cool and the contraction is read off on the manometer gauge. The hollow stopper is then twisted, so as to break the tube of turpentine, and after aborption of ozone is complete, the further contraction is read off.

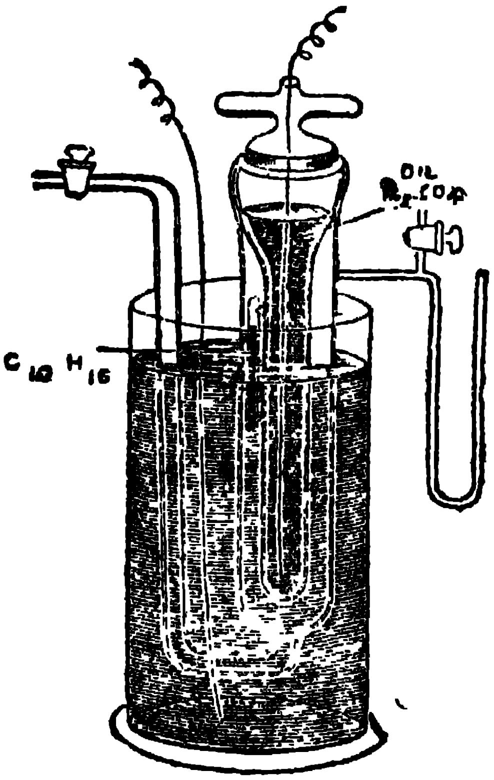


Fig. 51

Experimental Results :

1st contraction on ozonisation = x c. c.

2nd contraction on absorption of ozone by oil of turpentine = $2x$ c. c.

∴ Total diminution in volume of oxygen at the experiment $= 3x$ c. c.

And the volume of ozone formed $= 2x$ c. c.

Hence we conclude that 3 vols. of oxygen condense to give 2 volumes of ozone.

Deduction of Formula :

Let "*n*" be the number of molecules present in one volume of ozone. Then, by Avogadro's hypothesis, we get $3n$ molecules of oxygen condense into $2n$ molecules of ozone.

Or, 3 molecules of oxygen condense into 2 molecules of ozone. But 3 molecules of oxygen contain 6 atoms of oxygen (for oxygen molecule is diatomic). Thus 2 molecules of ozone contain 6 atoms of oxygen. Hence its molecular formula is O_3.

This molecular formula for ozone has been confirmed by the determination of vapour density of pure ozone by Riesenfeld. It has a density of 24 and so the molecular weight is 48, which tallies with the molecular formula O_3.

Also, on decomposition of ozone by heat, nothing but oxygen is obtained. Hence ozone is nothing but condensed oxygen.

Ozone, as indicated above, is nothing but condensed oxygen and as such is an allotropic modification of oxygen of the formula O_3. So all the chemical properties of oxygen are found to be present in ozone developed to a greater extent. The following reactions by which oxygen can be differentiated from ozone can be mentioned.—

(*i*) Freshly precipitated lead sulphide (black) is spread on a filter paper and treated with oxygen gas from a gas holder. No change in colour is noticed. When ozonised oxygen is passed over it, the black lead sulphide is changed to white lead sulphate.

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

(*ii*) Oxygen is passed through acidified KI solution. No iodine is liberated, but on passing ozonised oxygen through acidified KI solution iodine is liberated.

Q. 3. *How was fluorine isolated? Give a neat sketch of the apparatus employed. Describe the properties of fluorine and compare them with those of chlorine.*

Ans. Isolation of fluorine was carried out by Moissan by the electrolysis of a solution of potassium hydrogen fluoride, KF, HF in anhydrous hydrofluoric acid, HF. The apparatus consisted of a U-tube made of an alloy of Platinum-Iridium, provided with two side tubes and fitted with fluorspar stoppers. Two electrodes, made also of Platinum-Iridium alloy and thickened at the bottom, passed through the fluorspar stoppers. The whole apparatus was kept immersed in a bath of boiling methyl chloride at about—23°C. The U-tube was ⅔rd filled up with the electrolyte, a solution of KF, HF in anhydrous HF. On passing the current through the electrolyte HF underwent decomposition, H_2 being liberated at the cathode and fluorine at the anode. The fluorine was led through a spiral of platinum kept immersed in boiling methyl chloride to remove any HF vapour by condensation. The gas was next passed through a tube of platinum packed with NaF which removed the last trace of HF vapour. Fluorine, thus freed from HF vapour, was

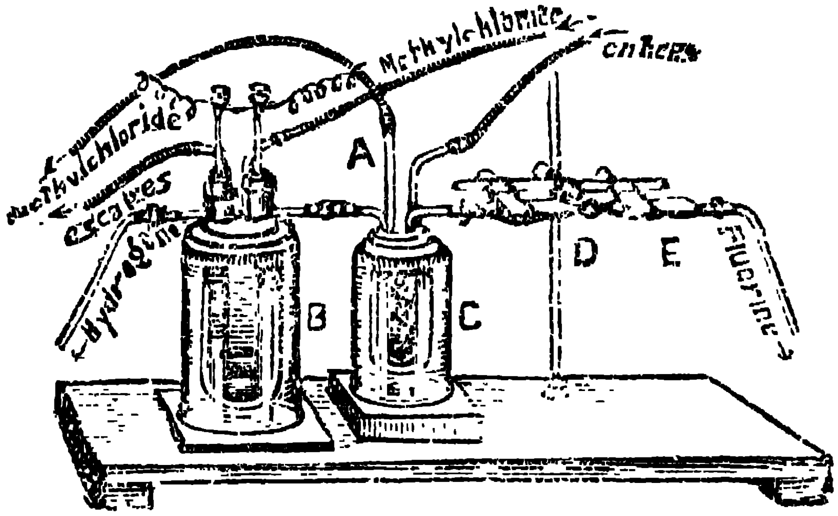


Fig. 52

originally absorbed by Moissan in moist iron nails, but could be collected in a platinum vessel by the upward displacement of air.

Comparison of Properties of Fluorine and Chlorine

Fluorine	Chlorine
1. At. wt.—19	1. At wt.—35·5
2. Physical State—Gas	2. Physical State—Gas
3. Colour—Pale yellow	3. Colour—Greenish yellow
4. Odour—Characteristic irritating smell	4. Odour—Pungent irritating smell.
5. Heaviness—slightly heavier than air.	5. Heaviness—2½ times heavier than air.
6. Solubility in water—Decomposes water with evolution of ozonised oxygen and formation of HF.	6. Solubility in water—Fairly soluble. The solution is called chlorine water.
7. Action on animals—Poisonous, attacks mucous membrane of the throat and the nose.	7. Action on animals—Poisonous, attacks mucous membrane of the throat and the nose.
8. Compounds with oxygen—One definite oxide known, F_2O, obtained by indirect combination with O_2. Another oxide, F_2O_2 has also been recognised.	8. Compounds with oxygen—Several unstable oxides known, Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7, all obtained by indirect combination with O_2.
9. Action with Hydrogen—The mixture with hydrogen explodes even in the dark and at low temperatures forming HF.	9. Action with Hydrogen—The mixture with hydrogen explodes when exposed to direct sunlight forming HCl.

Fluorine	Chlorine
10. Bleaching action—Has destructive action on vegetable colouring matter.	10. Bleaching action—Bleaches vegetable colour in presence of water.
11. Chemical activity—Most active element known.	11. Chemical activity—Less active than fluorine.
12. Properties of calcium salt—White, crystalline, *insoluble.*	12. Properties of calcium salt—White, crystalline, *soluble.*
13. Properties of silver salt—White *soluble.*	13. Properties of Ag-salt—White *insoluble.*

Q. 4. *Explain, giving examples, what is meant by* **oxidation** *and* **reduction.** *Describe experiments to illustrate the oxidising properties of manganese dioxide and bromine, as well as the reducing properties of sulphur dioxide and sulphuretted hydrogen.*

Ans. Oxidation is defined as the process in which there is an increase in the proportion of oxygen or of an electro-negative element or radical in an element or a compound, or in which there is a decrease in the proportion of hydrogen or of an electro-positive element or radical in a compound.

Reduction is defined as the process in which there is an increase in the proportion of hydrogen or of an electro-positive element or radical in an element or a compound, or in which there is a diminution in the proportion of oxygen or of an equivalent electro-negative element or radical in a compound.

Thus reduction is the reverse of oxidation.

Thus when sulphur is burnt in oxygen, it is oxidised to sulphur dioxide.

$$S + O_2 = SO_2.$$

When iron is heated in a stream of chlorine gas, it is oxidised to ferric chloride.

$$2Fe + 3Cl_2 = Fe_2Cl_6.$$

When hydrochloric acid is heated with manganese dioxide, it is oxidised to chlorine by removal of hydrogen.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

Similarly, when hydrogen peroxide is added to potassium iodide, iodine is liberated and thus potassium iodide is oxidised.

$$2KI + H_2O_2 = 2KOH + I_2.$$

When hydrogen gas is passed over heated copper oxide (black), it is reduced to metallic copper (red) by removal of oxygen.

$$CuO + H_2 = Cu + H_2O.$$

When sulphuretted hydrogen is passed into iodine suspened in water, iodine is reduced to hydriodic acid by addition of hydrogen.

$$H_2S + I_2 = 2HI + S.$$

When ferric chloride solution (yellow) is treated with zinc and hydrochloric acid, it is reduced to ferrous chloride (solution colourless) by nascent hydrogen.

$$FeCl_3 + H = FeCl_2 + HCl.$$

When metallic potassium is heated in chlorine gas, chlorine is reduced to potassium chloride.

$$2K + Cl_2 = 2KCl.$$

Oxidation will be seen to denote, from what has been said, an increase in the active valency of the central atom, as for example, when ferrous chloride is oxidised to ferric chloride, or stannous chloride is oxidised to stannic chloride.

From ionic standpoint, if we take into consideration the reaction,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

it can be represented as

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised by the loss of two electrons which have passed to the ferric ions, reducing them to the ferrous state.

Hence, oxidation may be defined as a *loss of electrons* and reduction as a gain in electrons.

Oxidising properties of *manganese dioxide* and *bromine* :—

Expt. Heat concentrated hydrochloric acid with Manganese dioxide. Chlorine is evolved. Thus, by removal of hydrogen from hydrochloric acid, the hydrochloric acid is oxidised to chlorine. Hence manganese dioxide oxidises hydrochloric acid.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

Expt. Take a little quantity of bromine water in a beaker and pass sulphuretted hydrogen gas through it. Sulphur separates. Sulphuretted hydrogen is oxidised, by removal of hydrogen, to sulphur. Thus bromine acts as an oxidising agent.

$$H_2S + Br_2 = 2HBr + S.$$

Reducing properties of *sulphur dioxide* and *sulphuretted hydrogen.*

Expt. Pass sulphur dioxide gas through a solution of potassium permanganate acidified with dilute sulphuric acid. Potassium permanganate is reduced to manganous sulphate. The valency of manganese is reduced from 7 in permanganate to 2 in manganous salt and hence reduction is effected.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Expt. Pass H_2S gas through bromine water taken in a beaker. Sulphur separates and the colour of bromine is discharged through the formation of hydrobromic acid. Thus by the addition of hydrogen to bromine the reduction of bromine takes place.

$$H_2S + Br_2 = 2HBr + S.$$

Q. 5. *Define and illustrate* **any four** *of the following* :—

Decomposition, dissociation, electro-chemical equivalent, valency, dialysis, efflorescence and deliquescene.

Ans. *Decomposition* is a process in which there is a permanent breaking down of molecules of substances into simpler components under the influence of physical agency like heat, light etc., and the components do not recombine under changed or reversed conditions.

Thus when ammonium nitrate is heated it decomposes into water and nitrous oxide and the products of decomposition do not recombine on cooling.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Dissociation is a process of temporary splitting up of molecules of substances into simpler molecules or atoms under the influence of physical agency, which reunite under reversal of the physical conditions, the splitting taking place in such a fashion that a dynamic equilibrium is set up under all changed conditions between undecomposed molecules and the simpler compounds or elements formed from it.

Thus on heating, ammonium chloride dissociates into ammonia and hydrogen chloride and on cooling original ammonium chloride is reformed, but during heating an equilibrium condition is set up depending upon temperature, when rate of decomposition of NH_4Cl and of recombination of NH_3 and HCl formed is found to balance.

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

Similar thing happens on heating phosphorus pentachloride

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \text{ ; and of iodine,}$$
$$I_2 \rightleftharpoons I + I.$$

Electro-chemical equivalent of an ion or an element is that weight of it, in grams, which is liberated by the passage of one coulomb of electricity, *i.e.*, a current of one ampere flowing for one second through an electrolytic solution containing that ion or the element.

The electro-chemical equivalent of silver is 0·001118 gram, meaning thereby that one ampere of electric current flowing for 1 second through a solution of silver nitrate will liberate 0·001118 gram of silver at the cathode.

Valency of an element is defined as its combining capacity with other elements and is expressed as a number which indicates the number of hydrogen atoms or chlorine atoms with which one atom of the element can combine.

Thus taking the following compounds in consideration, viz., (*i*) hydrogen chloride, HCl ; (*ii*) hydrogen sulphide, H_2S ; (*iii*) phosphine, PH_3 and (*iv*) methane, CH_4, we find that in (*i*) one atom of chlorine combines with one atom of hyrogen, in (*ii*) one atom of sulphur combines with two atoms of hydrogen, in (*iii*) one atom of phosphorus combines with three atoms of hydrogen and in (*iv*) one atom of carbon combines with four atoms of hydrogen. So chlorine is considered to be monovalent, sulphur bivalent, phosphorus trivalent and carbon tetravalent.

Valency is at present considered to be of electrical origin and according to the octet theory it is defined as the tendency of an atom of the element mentioned to complete its octet in the outermost shell. Thus the atom of carbon with four electrons in the outermost shell strives to complete the octet in the outermost level either by accepting four electrons from other atom or atoms or by sharing four more electrons with atoms of other elements. Hence carbon is tetravalent. Sometimes an atom of an element lends all the electrons present in its outermost shell, thus exposing the completed octet in the penultimate shell. Thus sodium, which has one electron in the outermost level, transfers that one electron to chlorine and thereby exposes the completed octet of the penultimate shell. Thus sodium behaves as a monovalent element. Chlorine accepts that electron from sodium and thereby completes its outermost octet. Chlorine also thus behaves as a monovalent element.

Dialysis is the process by which a crystalloid is separated from a colloid by means of a semipermeable membrane which is capable of allowing the crystalloid molecules to pass through it, but not the colloid particles.

Graham found that certain substance like gum, albumen, silicic acid, etc. in solution could not pass practically through parchment, animal bladder, etc., whereas certain other substances like hydrochloric acid, common salt, nitre, etc., in solution readily passed through the parchment, animal bladder, etc.

Thus a shallow bell jar open at both ends, but fitted with a piece of parchment paper or bladder, is kept partly immersed in water in another jar. Into the bell jar aqueous solution of sodium chloride or potassium iodide is taken along with certain quantity of starch also in solution. After a time it is found that sodium chloride or potassium iodide has passed into the outer jar but particles of starch in solution is held back in the bell jar.

The apparatus thus used is called a dialyser, and this process of separation of starch from potassium iodide or sodium chloride is called dialysis.

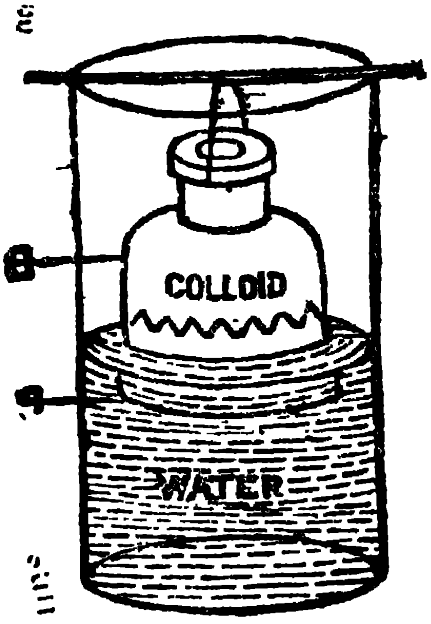


Fig. 53

Efflorescence is the phenomenon observed when certain crystalline substances in the solid state containing water of crystallisation lose their crystalline character by losing water and fall to powder when exposed to the atmosphere, *e.g.*, crystals of washing soda, $Na_2CO_3, 10H_2O$, lose 9 molecules of water when exposed to air and fall to powder giving Na_2CO_3, H_2O.

Deliquescence is the phenomenon observed when certain solid salts, on exposure to air absorb moisture from air and become moist, eventually turning into liquid, *e.g.*, calcium chloride, magnesium chloride, etc.

Q. 6. *What is the difference in chemical composition and physical properties between cast iron, wrought iron and steel? State their respective uses.*

Describe two important methods by which steel is prepared from cast iron.

Ans. The main point of difference between cast iron, wrought iron and steel is in carbon content. Cast iron contains 2—5% of carbon as also other impurities like S, P, Si, Mn, etc.; wrought iron contains no other impurity except carbon and that also to the minimum extent, viz., 0·12 − 0·5%; steel contains carbon to the extent of 0·25 to 1·5%. Thus steel is intermediate in composition between cast iron and wrought iron. Wrought iron is the purest form of commercial iron, whereas elements other than carbon are intentionally introduced in steel for modifying its properties.

The main points of difference in physical properties are enumerated in the following table :—

Physical properties.	Cast iron.	Wrought iron.	Steel
1. Melting point.	1200°C.	1500°C	1300° – 1400°C.
2. Brittleness or Malleability	Brittle	Malleable	Malleable and Brittle.
3. Hardness.	Hard	Soft	Hard and soft.
4. Structure.	Crystalline.	Fibrous.	Crystalline.
5. Tempering.	Cannot be tempered.	Can be tempered.	Can be tempered.
6. Forging and welding.	Cannot be forged or welded.	Cannot be forged and welded.	Can be forged and welded.
7. Magnetisation.	Cannot be permanently magnetised.	Cannot be permanently magnetised.	Can be permanently magnetised.
Uses :—	For articles produced by casting ; and for the manufacture of steel and wrought iron.	In the manufacture of articles required in husbandry in the manufacture of railway lines, locomotives, joists, cranes etc., in the manufacture of surgical instruments cutlery, etc.	In the preparation of *cores* of electro-magnets ; piano-wires, and wire-netting.

The two important methods by which steel is prepared from cast iron are (*a*) Bessemer Process, both acid and basic, and (*b*) Open Hearth Process, both acid and basic.

Bessemer Process :—At the present time major portion of steel, in the first stage of production of sulphur-free steel, is produced by the Bessemer process. The process consists, in oxidising the impurities present in cast iron, by blowing a blast of air through the molten metal. The operation is carried out in a large pear-shaped vessel made of wrought iron plates rivetted together, known as a *converter.* It is mounted on trunnions, so that the converter can be tilted in any position either vertical or horizontal, with its help. An air-chamber is fitted to the base, and through this air-chamber a powerful blast of air can be admitted. The converter is lined either with siliceous material (in acid Bessemer process) when the cast iron is free from phosphorus, or with burnt dolomite or magnesite (in basic Bessemer process) when phosphorus is present as impurity in cast iron.

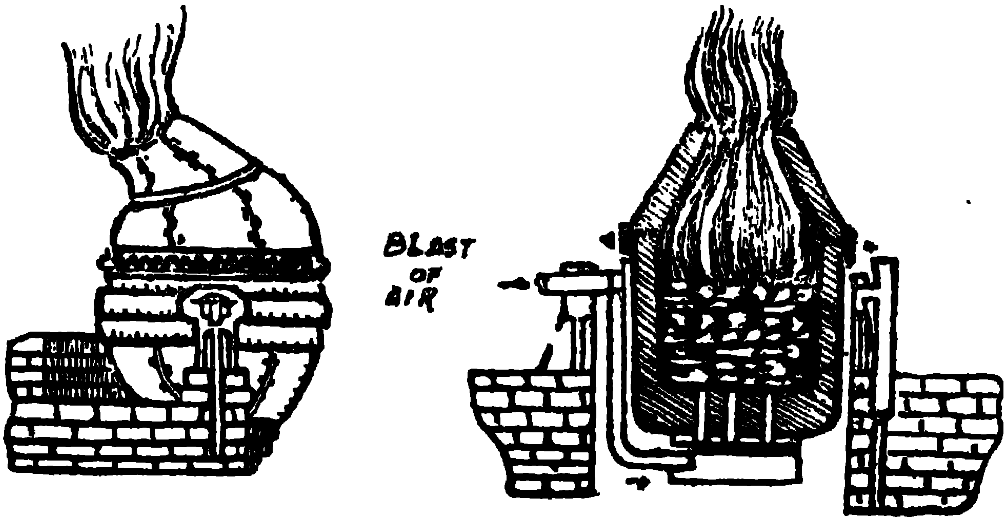


Fig. 54

The converter is first tilted into the horizontal position and a quantity of molten cast iron directly from the blast furnace is run in. The blast of air is then started and the converter immediately swung back into a vertical position. Within a very short time the whole of the impurities are burnt away. The completion of the operation is sharply marked by the sudden disappearance of the flame from the open mouth of the converter.

The blast is stopped at this stage in the *acid* Bessemer process, but in the *basic* Bessemer process, the blast is continued for a few minutes even after the dropping of the flame and it is stated that during this after-blow phosphorus is removed. The converter is then once more tilted into a horizontal position and an exact quantity of molten *spiegeleisen* (a mixture of C, Fe and Mn, containing about 20% Mn) is then added (in the *acid* process) to recarburize the metal ; the blast of air is then turned on for a few moments inorder to mix the materials thoroughly. Next the contents are poured out into ladles. In case of phosphatic cast-iron spiegeleisen is added after pouring the molten charge on to ladles.

The reactions that occur are : Silicon is first attacked and oxidised to silica, SiO_2. Manganese present in cast-iron is then oxidised to MnO and this MnO and SiO_2 combine to form manganese silicate, a slag. Iron is then attacked and the oxide of iron formed attacks carbon producing carbon monoxide. This carbon monoxide burns at the mouth of the converter with sparks produced from iron burning to a certain extent. The heat produced from the oxidation of silicon to silica maintains the mass in molten condition. In the basic process, phosphorus is oxidised at the end of the operation during the afterblow into P_2O_5 and this P_2O_5 combines with the MgO and CaO of the lining, forming phosphates which are removed as slag and used as manure. In the basic process some lime is also added along with the charge of cast-iron inorder to keep the slag basic.

Open Hearth Process :—Molten cast iron is run into the bed of the open hearth furance which is of the Reverberatory type, with the *regenerator* system fitted at the bottom. It is lined either with siliceous matter (*acid* process) or with burnt dolomite or magnesite (basic process). The furnace is heated with the help of producer gas.

The producer gas and air are strongly heated before being burnt by coming in contact with chequered brick-work, R_1 and R_2, say, as shown in the figure, which are called regenerators and are heated by the hot waste gases of the furnace as shown in the figure. In the meantime two other such brick-work chambers R_3 and R_4 are heated by hot waste gases of the furnace. When R_1 and R_2 cools down, producer gas and air are then turned on to R_3 and R_4 and after being pre-heated are burnt and hot waste gases are now made to pass over R_1 and R_2 thus heating them. Thus the chambers R_1, R_2, R_3 and R_4 act as heat-regenerators. Scarp steel and pure haematite are now added at intervals to molten cast iron on the hearth. Haematite

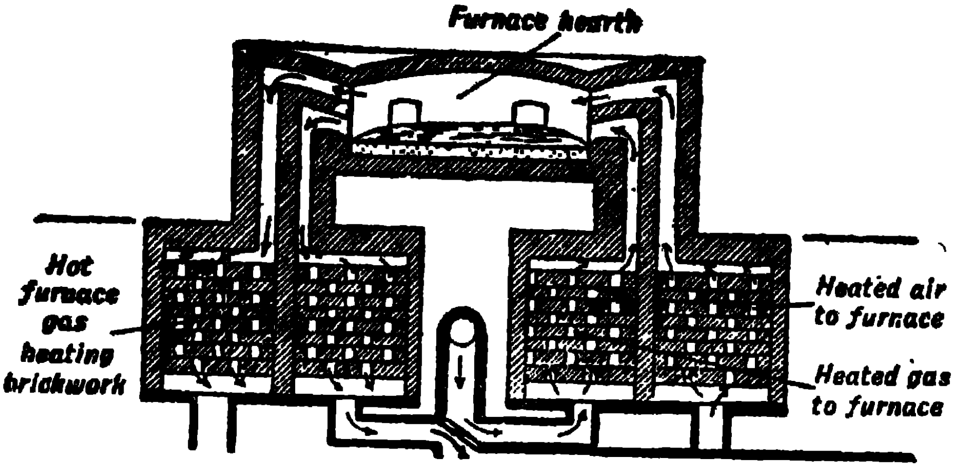


Fig. 55

hastens the decarburisation of cast iron. When all the impurities are burnt away, *Spiegel* is added in requisite amount to recarburise the iron. Afterwards the molten steel is run off by tilting the hearth and is cast into ingots.

Q. 7. *Give the formula of the following substances. Describe their preparation and state their uses.*

(*a*) *Bleaching powder*, (*b*) *calomel*, (*c*) *corrosive sublimate*, (*d*) *green vitriol*, (*e*) *white lead.*

Ans. (*a*) Bleaching powder—$Ca(OCl)Cl$.

For the preparation of bleaching powder with the use of Deacon's chlorine which contains only 8% of chlorine by volume, Hascenclever's screw chamber is employed. It is made of several horizontal iron tubes placed one above the other and joined at the ends. The upper tube is provided with a hopper for feeding in lime and there is an Archimedien screw arrangement by means of which the lime can be pushed on. The slaked lime, $Ca(OH)_2$, containing not more than 4% of water, is fed in through the hopper and pushed on gradually through the several tubes of the system. Chlorine is admitted at the open end of the lowermost tube. In this way chlorine and slaked lime is made to come into intimate contact and a very good bleaching powder is produced.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

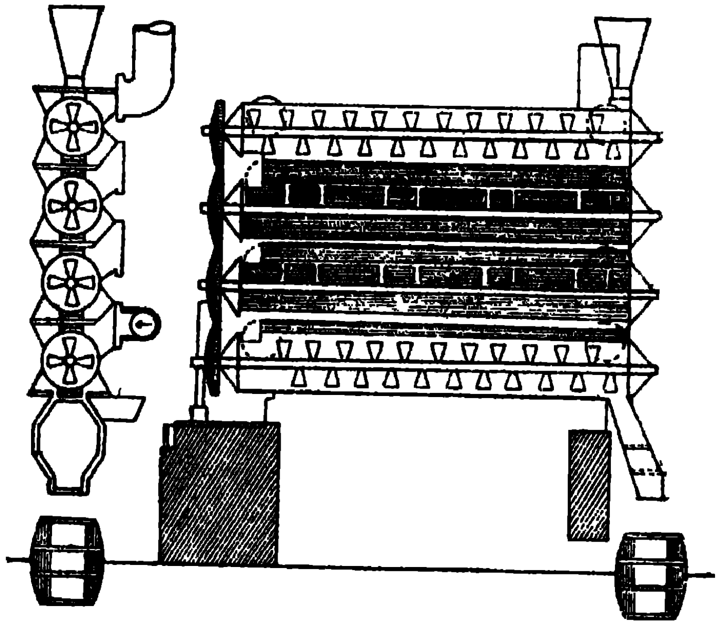


Fig. 56

The bleaching powder formed is discharged at the end of the lowermost tube and is collected in iron drums which are sealed when full and sent out to the market.

Bleaching powder is *used* as an oxidising, bleaching and chlorinating agent. It is also used as a disinfectant. It has also germicidal properties and so employed in the sterilisation of water.

(*b*) Calomel—Hg_2Cl_2.

Mercurous chloride (*Calomel*), Hg_2Cl_2, is obtained as a curdy white precipitate when the solution of a soluble mercurous salt is treated with HCl or with the solution of a chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 + 2NaNO_3.$$

This substance is manufactured by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel. Hg_2Cl_2 sublimes off and condenses as a white cake in the upper part of the vessel. The sublimate is taken out and repeatedly boiled with water to free it completely from unchanged mercuric chloride, filtered and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Use. Calomel is used in medicine as a purgative.

(*c*) Corrosive sublimate—$HgCl_2$.

Corrosive sublimate (mercuric chloride) is prepared by heating a mixture of mercuric sulphate and common salt in long-necked flat-bottomed flasks made of burnt clay on a sand bath.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

A little MnO_2 is added to prevent the formation of any mercurous chloride by the reducing action of organic matter present in common salt. After the reaction the flasks are cooled and then broken and the cake of mercuric chloride condensed on the upper part is removed. It is purified by crystallisation from hot water solution.

Corrosive sublimate is used in medicine as an antiseptic, in dressing skins, furs, etc., and also as a reagent in the laboratory.

(*d*) Green vitriol, $FeSO_4, 7H_2O$.

Piano-wire, which is made of wrought iron, is dissolved in dilute sulphuric acid, the solution is filtered and the filtered solution is concentrated by evaporation, out of contact with air, till the crystallisation point is reached.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

On cooling crystals of green vitriol, having the composition $FeSO_4, 7H_2O$, separate out.

Uses.—Green vitriol or Ferrous sulphate heptahydrate, is used in the preparation of writing ink ; in the manufacture of *rouge* : in dyeing industry ; and in medicine.

(*e*) White lead, $2PbCO_3, Pb(OH)_2$.

Manufacture of White lead by the Dutch Process :—

Pieces of lead are placed in earthen-ware pots having perforated shelves near the bottom, on which lead rests. Dilute acetic acid (vinegar) is taken in the pots.

The pots are now placed, one above the other, with alternate layers of spent tan-bark or horse-dung, inside a shed, the lower pots being covered with planks of wood on which horse-dung or spent tanbark rests, and the whole stack is left as such for about 6 to 8 weeks.

Spent tan-bark or horse-dung undergoes fermentation ; CO_2

is formed, and the heat generated volatilises acetic acid which attacks lead giving basic lead acetate. Basic lead acetate is now decomposed by CO_2, producing basic lead carbonate (white lead) and acetic acid. The acid attacks more lead converting it into white lead and the cycle of changes is repeated. When all the lead is used up, the pots are taken down, the crust of white lead is detached, and is finely ground to separate it from any unchanged lead. It is now washed well with water and dried.

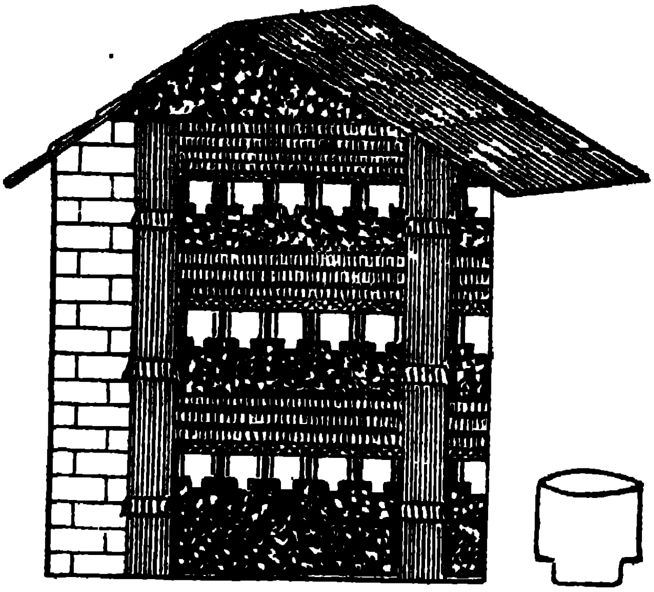


Fig. 57

Reactions :—Horse dung or tan-bark serves *two* purposes :—(*i*) by putrefaction it keeps the pots warm, and thus acetic acid is volatilised, and (*ii*) it evolves CO_2 which converts basic lead acetate into basic lead carbonate. According to the more recent theory about the reaction occurring in this process, lead is converted into $Pb(OH)_2$ by the moisture and oxygen of the air. Acetic acid dissolves $Pb(OH)_2$ giving lead acetate which with more $Pb(OH)_2$, forms basic lead acetate. Basic lead acetate, thus formed, reacts with CO_2 giving white lead and acetic acid back, which again converts more lead into basic lead acetate. Thus the process works in a cycle.

(1) $2Pb + 2H_2O + O_2 = 2Pb(OH)_2$

(2) $Pb(OH)_2 + 2CH_3COOH = Pb(CH_3COO)_2 + 2H_2O$

(3) $Pb(CH_3COO)_2 + Pb(OH)_2 = Pb(CH_3COO)_2, Pb(OH)_2$.

(4) $$3[Pb(CH_3COO)_2, Pb(OH)_2] + 2H_2O + 4CO_2 = 2[2PbCO_3, Pb(OH)_2] + 6CH_3COOH.$$

Use :—White lead is used as a white pigment along with linseed oil either for oil-painting or for covering wooden structure.

Q. 8. *Explain, giving equations what happens when :*

(*a*) *Sulphur is heated with concentrated sulphuric acid ;*

(*b*) *Carbon dioxide is passed through lime water till saturation and the mixture subsequently boiled ;*

(*c*) *Chlorine is passed through a solution of sulphur dioxide :*

(*d*) *Ammonia is added to a solution of mercuric chloride.*

Ans. (*a*) When sulphur is heated with concentrated sulphuric acid, sulphur dioxide is evolved as gas and water is produced. $S + 2H_2SO_4 = 3SO_2 + 2H_2O.$

Here sulphur is oxidised by sulphuric acid to sulphur dioxide and sulphuric acid is reduced at the same time to sulphur dioxide.

(*b*) When carbon dioxide is passed through lime water till saturation, calcium carbonate, which is first formed as a white precipitate, dissolves forming calcium bicarbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

white ppt.

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

Soluble bicarbonate of calcium.

Then when the mixture is subsequently boiled, calcium bicarbonate decomposes, evolving carbon dioxide and depositing insoluble calcium carbonate as a white precipitate.

$$CaH_2(CO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

white ppt.

(*c*) When chlorine is passed through a solution of sulphur dioxide, sulphuric acid is formed through the oxidation of sulphur dioxide and chlorine is reduced to hydrochloric acid. So ultimately we get a mixture of sulphuric acid and hydrochloric acid.

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

(*d*) When ammonia is added to a solution of mercuric chloride, a white precipitate—called *infusible white precipitate* (NH_2HgCl) is formed along with hydrochloric acid and water.

$$HgCl_2 + NH_4OH = NH_2HgCl + HCl + H_2O.$$

SECOND PAPER—1948

Q. 1. *Describe experiments by which you can prove that there are at least two atoms of hydrogen in a molecule of water.*

Ans. When metallic sodium is thrown into water in small bits, hydrogen is evolved and a solution is obtained which is found to be soapy to the touch and is caustic and turns red litmus blue. It is a solution of sodium hydroxide. The reaction is usually represented by the equation

$$2Na + 2H_2O = 2NaOH + H_2$$

Sufficient quantity of sodium is allowed to react with the water taken so that all the water has been used up and we have only caustic soda present.

Then the resulting substance, that is, caustic soda, is heated with metallic zinc. Hydrogen is again evolved as gas and a substance is formed which, on analysis, is found not to contain any hydrogen. The reaction is usually represented by the equation,

$$2NaOH + Zn = Na_2ZnO_2 + H_2.$$

Thus, it is found from the above experiments that hydrogen present in water can be expelled in two instalments from it. Hence it is inferred that water contains at least two atoms of hydrogen.

Q. 2. *How is sulphur dioxide prepared ? State its properties. How would you determine its gravimetric composition ?*

Ans. In the laboratory, sulphur dioxide is prepared in the following way :—Some copper turnings are taken in a flask fitted with a thistle funnel and a delivery tube. Concentrated H_2SO_4 is poured down the thistle funnel till the end of the funnel remains dipped under the surface of the acid. The flask is then placed on a piece of wire gauze and heated till the gas begins to be evolved. The source of heat is then removed and the gas is collected by the upward displacement of air. The gas is fairly dry and pure, but may be further dried by passing through a wash bottle containing concentrated sulphuric acid and collected over mercury.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Properties of sulphur dioxide :—

Sulphur dioxide is a colourless gas with a suffocating odour of burning sulphur. It is heavier than air and extremely soluble in water. The gas can be easily liquefied. The gas is neither combustible nor ordinarily a supporter of combustion. But heated metallic potassium burns in it.

$$4K + 3SO_2 = K_2SO_3 + K_2S_2O_3.$$

Potassium sulphite Potassium thiosulphate.

Lead peroxide, when heated and introduced into the gas, becomes incandescent and lead sulphate is formed,

$$PbO_2 + SO_2 = PbSO_4.$$

The solution of sulphur dioxide in water is acidic and perhaps contains sulphurous acid. $H_2O + SO_2 = H_2SO_3$. The acid cannot be isolated, for, on boiling, SO_2 escapes and water remains behind. When a solution of SO_2 is heated in a sealed tube to 150°C., sulphur separates and renders the solution opalescent.

$$3H_2SO_3 = S + 2H_2SO_4 + H_2O.$$

Sulphur dioxide is a powerful reducing agent. It reduces ferric salts to ferrous salts ; chlorine, bromine and iodine to their hydracids, as also acidified permanganate and dichromate solutions.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl$$
$$Cl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl$$
$$I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI.$$
$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$
$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

It can bleach vegetable colouring matter in presence of moisture and the bleaching takes place either through the agency of nascent hydrogen by reduction or by direct addition of sulphur dioxide to the colouring matter. Under certain circumstances sulphur dioxide can act as an oxidising agent, for example, it oxidises sulphuretted hydrogen to sulphur—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

Gravimetric composition of sulphur dioxide :—

The method for the determination of the gravimetric composition of sulphur dioxide is exactly the same as that used for determining the gravimetric composition of carbon dioxide, for which see p. 79, Q. 3, First Paper, 1943. The difference is that instead of pure sugar charcoal a sample of pure sulphur is to be taken in the porcelain boat. The product of combustion is sulphur dioxide and this is absorbed by the caustic potash solution in the potash bulb. It is found by actual experiment that 32 parts by weight of sulphur combine with 32 parts by weight of oxygen to form 64 parts by weight of sulphur dioxide. But 64 is the molecular weight of sulphur dioxide, because the experimentally determined value for its density relative to hydrogen is 32. Now 32 stands for 1 atom of sulphur and 32 in case of oxygen stands for two atoms of oxygen, since the atomic weight of oxygen is 16. Thus, in 1 molecule of sulphur dioxide there are 1 atom of sulphur and 2 atoms of oxygen and therefore the formula for sulphur dioxide is SO_2.

[*N. B. This method does not give accurate results and so is never followed.*]

Q. 3. *How would you convert*

(*a*) *Carbon dioxide into carbon monoxide and* vice versa.

(*b*) *Nitrogen into ammonia and* vice versa.

(*c*) *Chlorine into hydrochloric acid and* vice versa.

Ans. (*a*) By passing carbon dioxide over a bed of red-hot charcoal, it can be converted into carbon monoxide.

$$CO_2 + C = 2CO.$$

That CO has been formed is proved by the fact that the gas burns with a lambent blue flame and is absorbed by HCl-solution of CuCl. When carbon monoxide is set fire to, it burns to carbon dioxide.

$$2CO + O_2 = 2CO_2.$$

That carbon dioxide has been formed is proved by the fact that it extinguishes a lighted taper and turns lime-water milky.

(*b*) One volume of nitrogen is mixed with three volumes of hydrogen and the mixture is compressed to 200 atmospheric pressure and passed over an iron catalyst, with molybdenum as promoter heated electrically to a temperature of 550° – 700°C. Partial conversion into ammonia takes place.

$$N_2 + 3H_2 = 2NH_3.$$

Ammonia formed is absorbed in water. That ammonia has been formed is proved by the smell, by the production of dense white fumes with conc. HCl and red litmus being turned blue by the solution.

Ammonia gas is passed over heated copper oxide placed in a hard glass tube, ammonia gas being admitted at one end of the tube and the gas issuing at the other end being collected by displacement of water.

$$3CuO + 2NH_3 = 3H_2O + 3Cu + N_2.$$

That the gas is nitrogen is proved by the facts that it extinguishes a lighted taper, does not turn lime-water milky and is absorbed by heated magnesium.

(*c*) Chlorine gas is mixed with an equal volume of hydrogen and the mixture is exposed to a flash of burning magnesium ribbon. The gases combine with an explosion. The greenish-yellow colour of chlorine has disappeared, and the resulting gaseous product is dissolved in water.

$$H_2 + Cl_2 = 2HCl.$$

That hydrochloric acid has been produced is proved by the facts that the gaseous product is extremely soluble in water and that the solution turns blue litmus red. Also the solution gives a curdy white ppt. with $AgNO_3$ solution, insoluble in HNO_3 but soluble in dilute ammonia solution.

Hydrochloric acid is mixed with manganese dioxide and the mixture is heated. Greenish-yellow chlorine gas is evolved.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

That the gas evolved is chlorine is proved by its greenish-yellow colour and its peculiar odour like that of bleaching powder.

Q. 4. *What are the main features of the periodic classification of the elements ? Indicate some of its important applications.*

Ans. The main features of the periodic classification are that in it elements are arranged in the order of their increasing atomic weights and thereby certain striking regularities are observed. Mendeleeff stated the regularities as a Law, known as Periodic Law which runs thus : "The physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights." Mendeleeff arranged the elements known at his time according to their increasing atomic weights in a table, the elements being placed by him in horizontal rows and vertical columns. In arranging the elements Mendeleeff took into consideration the chemical similarity between elements and he arranged the chemically similar elements in the same vertical columns, called by him Groups. In this way elements were arranged by him in 8 vertical Groups, numbered I to VIII. To this, after the discovery of the inert gases of the atmosphere, another group was added and named Group O. Afterwards Mendeleeff subdivided each group into two sub-groups, sub-group A and sub-group B, depending upon chemical similarity.

The horizontal rows were called by him Periods. The original numbering of Periods by Mendeleeff has undergone a thorough change and in the modern Periodic arrangements we have Period 1 consisting of two elements, Hydrogen and Helium ; Period 2 consisting of 8 elements from Lithium to Neon ; Period 3, also consisting of 8 elements from Sodium to Argon. These are known as *short periods*. Period 4 contains 18 elements starting from Potassium upto Krypton ; Period 5 also consists of 18 elements, starting from Rubidium and ending in Xenon. These two periods are called *long periods*. Period 6 consists of 32 elements and contains 15 rare-earth elements in a cluster in Group III ; this period is called *very long period*. Period 7 contains 6 radio elements, starting from the alkali metal analogue Frankium and ending in Uranium ; it is called a *fragmentary period*.

By this periodic arrangement of elements, certain regularities in physical and chemical properties of elements are brought to light. Elements belonging to the same sub-group show similarities and gradations in properties, both physical and chemical. Also as we pass on from element to element in a particular period, the physical properties like melting point, boiling point, atomic volume show periodic waxing and waning. Also such chemical properties as electro-chemical character and valency show regularities and return more or less to the same value in different periods under the same groups.

Applications of periodic classification :—

(1) Periodic classification of elements has systematised the study of Inorganic chemistry by rendering the study of 92 different elements into a study of 9 vertical columns.

(2) It has helped in the correction of doubtful atomic weights. For example, the atomic weight of Indium was

taken to be 76, being the second multiple of its equivalent weight 38, the valency of Indium being taken to be 2. But with that atomic weight Indium could not be accomodated in the periodic classification. Mendeleeff considered its chemical properties and suggested that the atomic weight of Indium was 114, being the third multiple of its equivalent weight, its valency being 3. The subsequent determination of the atomic weight of Indium corroborated this change.

(3) It has helped in the prediction of existence of hitherto unknown elements with their properties. Thus Mendeleeff had to leave *blank spaces* in certain parts of his periodic table inorder to maintain chemical analogy. He stated that the elements occupying those places were not known, but some day those elements could be discovered. He named those elements with the prefix *eka*—and predicted their properties. Thus he was led to name the elements belonging to Group III and occurring beneath boron and aluminium as eka-boron and eka-aluminium and stated their properties as the mean of those elements surrounding them on four sides. These elements were subsequently discovered and named Scandium and Gallium and the properties predicted by Mendeleeff were found to be associated with them.

(4) It has helped in the furtherance of chemical research by suggesting new analogies to be verified by experiments.

Q. 5. *How is phosphorus obtained on a large scale? What are its uses?*

How is phosphine prepared? Compare and contrast its properties with that of ammonia.

Ans. Naturally-occurring calcium phosphate is now-a-days utilised for getting phosphorus on a large scale. A mixture of a phosphate, sand and coke is fed through feed-hopper into a closed electric furnace made of brick-work provided with an outlet above for letting out the gases and phosphorus vapour, a slag hole at the bottom and carbon electrodes fitted a little above the bottom of the furance, an electric arc being struck between these carbon electrodes, producing a very high temperature.

The silica of the sand reacts at the high temperature of the furnace with calcium phosphate producing calcium silicate and phosphorus pentoxide, P_2O_5.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

The vapour of P_2O_5 is then reduced by carbon and carbon monoxide is formed and phosphorus is set free and is vapourised by the heat prevailing in the furnace.

$$P_2O_5 + 5C = 2P + 5CO.$$

Calcium silicate melts and sinks to the bottom from where it is run off through the slag hole. Phosphorus vapour and carbon monoxide escape through the outlet near the top and are passed into water where phosphorus vapour condenses and carbon monoxide, being insoluble in water, escapes as gas. Fresh mixture is introduced through the feed-hopper and the process is continuous.

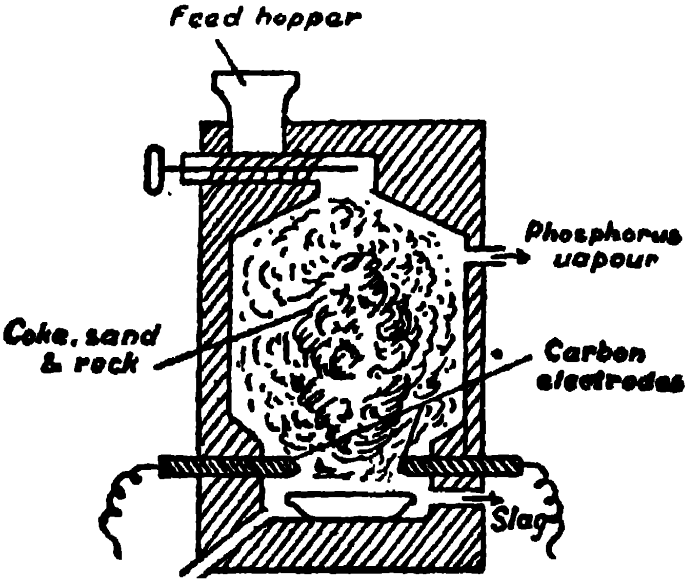


Fig. 58

Uses :—Phosphorus is largely used in the manufacture of matches. The head of the common *lucifer match* is composed of *white* P, mixed with KNO_3 or some other oxidising agent. Such matches are now-a-days supplanted by *safety matches*, the heads of which contain oxidising agents but no phosphorus. These ignite when rubbed on a surface coated with *red* phosphorus.

White phosphorus is also used in the preparation of P_2O_5 and of red phosphorus. Red phosphorus again is used in the laboratory for the preparation of HBr and HI as also in the preparation of phosphoric acid. A little amount is also used in making phosphor bronze, and as a rat-poison.

Preparation of phosphine :—

A flask, provided with an inlet tube reaching nearly to its bottom and a delivery tube, is taken. The inlet tube is connected with a laboratory gas-tap or a hydrogen-generating Kipp's apparatus. The delivery tube is connected with a gas-wash bottle containing alcohol (not shown in the figure.) The exit tube from the wash bottle is connected to another delivery tube which is dipped under water in a pneumatic trough.

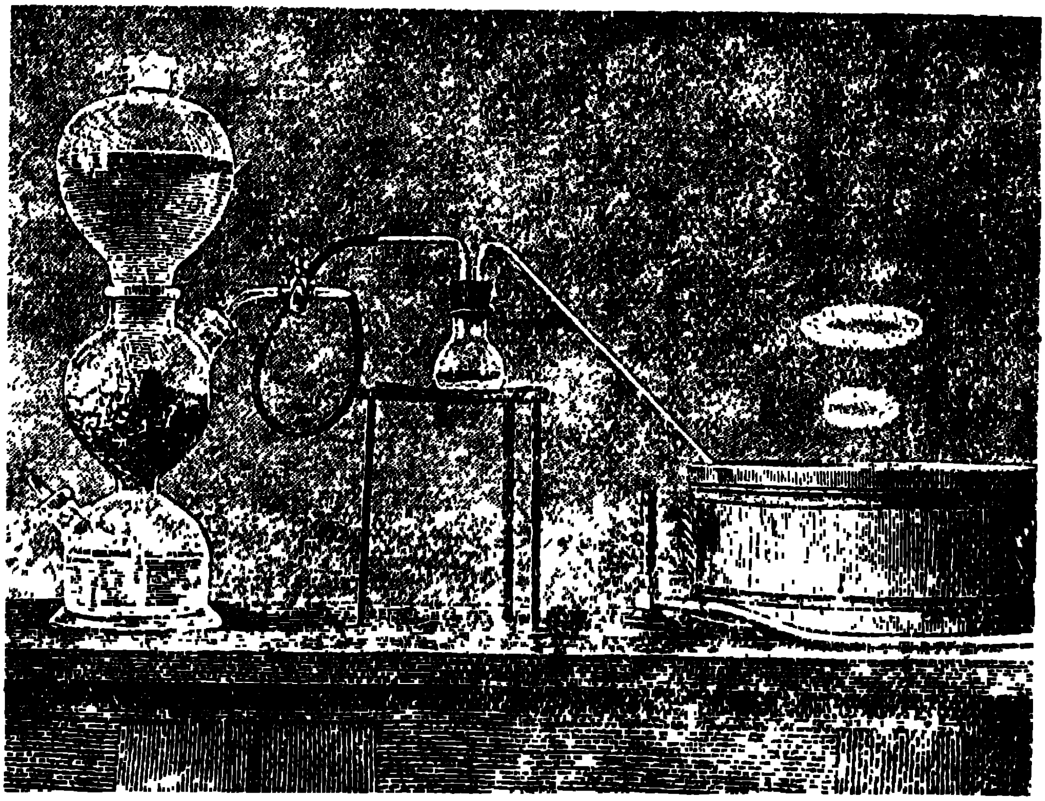


Fig. 59

A small quantity of white phosphorus and a 30 per cent. solution of caustic potash or caustic soda are taken in the flask. The air in the flask is then driven out by coal gas or hydrogen as the case may be ; otherwise explosion will take place. When all the air has been chased out, the flask is heated. Phosphine is produced, which is passed through a wash bottle containing alcohol and is collected in gas jars by displacement of water.

$$4P + 3NaOH + 3H_2O = \underbrace{3NaH_2PO_2}_{\text{Sodium hypophosphite}} + PH_3$$

Alcohol in the wash-bottle removes P_2H_4 which is also generated in the reaction, and which renders the gas spontaneously inflammable.

If, however, the gas be not washed with alcohol, and is allowed to bubble through water in the pneumatic trough, each bubble of the gas, as it comes out, catches fire and burns producing vortex rings of smoke as shown in the figure.

Comparison of Phosphine with Ammonia.

Phosphine, PH_3	Ammonia, NH_3
(1) It is a colourless gas, with the smell of rotten fish.	(1) It is a colourless gas, with a very pungent odour.
(2) It is heavier than air.	(2) It is lighter than air.
(3) It is poisonous.	(3) It is of non-poisonous nature.
(4) It is very slightly soluble in water ; the solution is non-alkaline and does not turn red litmus solution blue.	(4) It is extremely soluble in water ; the solution is alkaline and turns red litmus solution blue.
(5) Phosphine is feebly basic, and produces phosphonium compounds with halogen acids, specially under pressure. $PH_3 + HI = PH_4I$ etc.	(5) Ammonia is distinctly basic and gives ammonium compounds with halogen acids. $NH_3 + HI = NH_4I$ etc.
(6) It may be obtained by heating PH_4I with alkalies.	(6) It is obtained by heating ammonium salts with alkalies.

Phosphine, PH_3	Ammonia, NH_3
(7) Phosphine spontaneously burns in chlorine $PH_3 + 4Cl_2 = PCl_5 + 3HCl$ $PH_3 + 3Cl_2 = PCl_3 + 3HCl$	(7) Ammonia reacts with chlorine with evolution of heat and light giving N_2 and sometimes NCl_3, when Cl_2 is in excess. $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$ $NH_3 + 3Cl_2 = NCl_3 + 3HCl$
(8) When phosphine is passed into metallic salt solutions in water, phosphides of the metals are precipitated. $3CuSO_4 + 2PH_3 = 3H_2SO_4 + Cu_3P_2$	(8) When ammonia is passed into aqueous solutions of metallic salts, hydroxides of the metals, are usually precipitated. $CuSO_4 + 2NH_3 + 2H_2O = Cu(OH)_2 + (NH_4)_2SO_4$
	N.B. In excess of ammonia $Cu(OH)_2$ dissolves. $Cu(OH)_2 + 4NH_4OH = [Cu(NH_3)_4](OH)_2 + 4H_2O$ Deep blue solution.

Q. 6. *Name the principal ores of copper. How is the metal extracted from its ores? State the uses of the metal and that of its principal alloys.*

Ans. Important ores of copper are :—

(1) Ruby ore, Red copper ore or cuprite, Cu_2O.
(2) Copper glance, Cu_2S.
(3) Covellite or indigo copper, CuS.
(4) Copper pyrites, Cu_2S, Fe_2S_3 or $CuFeS_2$.
(5) Erythrite or purple copper ore, $3Cu_2S$, Fe_2S_3.
(6) Malachite, $CuCO_3$, $Cu(OH)_2$
(7) Azurite, $2CuCO_3$, $Cu(OH)_2$.

Copper can be extracted either from its oxide or carbonate ores as also from its sulphide ores. The method of extraction depends upon the nature of the ore. In the cases of the oxide and carbonate ores of copper, the ore is first subjected to a process of calcination, whereby cupric oxide is formed.

$$CuCO_3, Cu(OH)_2 = 2CuO + CO_2 + H_2O$$
$$2Cu_2O + O_2 = 4CuO.$$

The black oxide of copper so formed is then mixed with anthracite or coke and a little sand (acting as a fluxing material) and the mixture is heated strongly in a *blast furnace* whereby the oxide is reduced to the metal,

$$CuO + C = Cu + CO$$
$$CuO + CO = Cu + CO_2.$$

The flux (silica) combines with the impurities and form a fusible slag. The molten slag is run off and copper produced is taken out. Copper thus obtained is then refined by the *electrolytic process* described below.

From its sulphide ore, viz. copper pyrites, copper is extracted by thermal process.

(1) As the ore contains 4 to 5% of copper, a preliminary concentration is essential. The usual method employed is known as *oil-floatation process.* In this process the ore is first crushed and finely powdered. The powdered ore is next added to water containing a little pine oil, xanthate and lime and the mixture is churned by blowing air through the mixture. By this operation a froth is produced, which carries up along with it the particles of copper ore, these being preferentially wetted by oil, leaving sand and other impurities at the bottom, since these are preferentially wetted by water. The froth is collected by skimming and allowed to settle. By this means the concentration of copper in the ore is raised to 30 to 35%.

(2) The concentrated ore is next *roasted* in multiple-hearth furnace, the hearths being erected one above the other, so that the ore gradually decends from hearth to hearth. By this operation some of the sulphur in the ore is burnt to sulphur dioxide, which escapes as gas and the metals, viz., iron present in the ore and copper are partially oxidised.

$$Cu_2S, Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S, Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$

this last reaction occurring only to a very small extent.

(3) The roasted ore is next mixed with coke, sand (or slag

from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when the little quantity of Cu_2O formed in the previous operation reacts with the unchanged iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced during roasting operation reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained consisting of cuprous and ferrous sulphides is known as *matte.*

(4) The molten *matte,* mixed with a little sand,. is then directly run into a converter of the Bessemer type, but with this difference that the air-ports are situated a little above the bottom level. A blast of air is next introduced through the air-ports. Iron is first oxidised to ferrous oxide, FeO, which combines with the silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued, whereby Cu_2S is partially oxidised to Cu_2O. When two-thirds of the matte is thus oxidised, Cu_2O reacts with unchanged Cu_2S giving rise to metallic copper and sulphur dioxide. The slag is removed, the blast is stopped and the converter tilted to pour off molten copper. This copper, on cooling, is found to have a blistered appearance due to escape of sulphur dioxide and is known as "*blistered copper*",

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

(5) Blistered copper is now-a-days *refined* by an electrolytic method.

Thick blocks are made from blistered copper and are suspended from a metal rod into a bath of copper sulphate solution, acidified with 15% of sulphuric acid, and contained in a lead-lined wooden vat. The metal rod carrying these thick slabs is connected to the positive pole of a battery and is thus made the anode. Thin plates of pure copper are suspended in the same bath from another metal rod which in its turn is connected to the negative pole of the same battery and is thus made the cathode. These thin plates are so arranged that they are alternately inserted between the thick blocks. On passing electric current through the bath of copper sulphate, copper from the thick slabs is passed into solution as cupric ions and pure copper is deposited from the bath on the pure copper sheets serving as cathodes. Impurities present either pass into solution or are deposited at the bottom of the bath near the anodes as anode mud. Copper, thus obtained as a deposit on the cathode, is 99·99 per cent. pure.

Uses of copper :—Copper is used largely in electric industry—in electro-typing, for cables and wires for conveying electric current ; in the preparation of household utensils, for coinage and for the preparation of important alloys, like brass, bronze, German silver, etc.

Brass is an alloy of copper and zinc. It is used for making utensils, cartridge cases, etc.

Bronze is an alloy of copper and tin. It is used for making medals, statues, ornaments. It is also used in coinage, in which case it also contains zinc along with copper and tin.

German silver is an alloy of copper, zinc and nickel. It is used for preparing ornaments, utensils and other decorative articles.

Q. 7. *How you would test for the basic and acidic radicals in the following substances :—(a) Silver nitrate ; (b) Mercuric chloride ; (c) Zinc sulphate ; (d) Sodium iodide ; (e) Lead carbonate ?*

Ans. (*a*) Basic redical—**Silver.** (*i*) *Dry test.*—When a little of the substance is mixed with Na_2CO_3 and the mixture taken in a charcoal groove is heated in the *reducing* blow-pipe flame, a brilliant button of metallic silver is obtained. The button is found to be malleable, but it does not mark paper. It is soluble in HNO_3.

(*ii*) *Wet test.* When dil. HCl is added to a solution of the substance in distilled water, curdy white ppt. of AgCl is obtained. The precipitate does not dissolve in boiling water nor in conc. HNO_3, but dissolves readily in NH_4OH. This confirms Ag.

Dry test for nitrate.—A little of the salt is heated in a test-tube with conc. H_2SO_4 and copper turnings when brown fumes are evolved, With conc. H_2SO_4 alone no brown fumes are evolved—proving absence of bromide.

Wet test for nitrate.—A little quantity of water solution of the salt is taken in a test-tube and conc. H_2SO_4 is added to it. Then holding the test-tube in a slanting position under a tap of running water, a freshly prepared solution of ferrous sulphate is added to it. A brown ring appears at the junction of conc. H_2SO_4 and ferrous sulphate solution. The brown ring is due to NO being formed by reduction of HNO_3 by $FeSO_4$ and its subsequent absorption by $FeSO_4$ sol. forming $FeSO_4, NO$.

(*b*) Basic radical—**Mercury.** (*i*) *Dry test.*—The solid salt is intimately mixed with soda lime. The mixture is taken in a bulb-tube and then heated. A beautiful white mirror is produced in the upper colder part of the tube. On scratching with a glass rod, globules of mercury are formed and can be collected on a piece of paper.

(*ii*) *Wet test.*—To the solution of $HgCl_2$ in water, dil. HCl is added. The absence of any precipitate shows the absence of Pb, Ag or Hg (ous) salts. The acidified solution is then heated to boiling and through the hot solution H_2S is passed in slowly. At first a *white* ppt. is formed, which gradually becomes *yellow*, then *brown* and finally *black*. The black ppt. is filtered, washed and then dissolved in aqua regia. The excess of acid is destroyed by addition of Na_2CO_3 and then in the faintly acid solution a copper foil is placed. A grey deposit is formed on the copper foil, which turns white on rubbing under water. This confirms mercury.

Acidic radical—**Chloride.** (*i*) *Dry test.*—The solid salt is mixed with Na_2CO_3 and heated for a while. The residue is extracted with water and evaporated to dryness. This is mixed with MnO_2 and conc. H_2SO_4 in excess and heated, when chlorine is evolved which is recognised by its greenish yellow colour and odour like that of bleaching powder. (*ii*) *Wet test.*—To a solution of the substance in water $AgNO_3$ solution is added. A curdy white ppt. of AgCl is produced which is insoluble in conc. HNO_3 but soluble in NH_4OH. This confirms chloride.

(*c*) *Dry test for zinc* :—

A little quantity of the salt is taken on a charcoal block and heated strongly in the oxidising flame. An incandescent white mass is obtained. This is cooled and moistend with a drop or two of cobalt nitrate solution and heated again in the oxidising flame. A green mass is obtained known as *Rinmann's green*. This confirms the presence of zinc.

Wet test for zinc :—

A little of the salt is dissolved in water and then dil. HCl added. No ppt. indicates the absence of Gr. I metals. The solution containing HCl is then heated and H_2S passed in. No ppt. shows absence of Gr. II metals. H_2S is boiled off, a drop or two conc. HNO_3 added and the mixture boiled. Then solid NH_4Cl and then NH_4OH are added. No ppt. indicates absence of Gr. III-A metals. Then the ammoniacal solution is treated with H_2S. A white ppt. is obtained. The ppt. is filtered, washed and then dissolved in HCl, removing all H_2S by boiling. Then NaOH solution is added gradually. At first a white ppt. appears but this dissolves on addition of more NaOH. This confirms the presence of zinc.

Dry test for sulphate :—A little quantity of the salt is mixed with charcoal powder and taken in a groove made into a charcoal block. The mixture is next heated under the reducing blow-pipe flame. The residue is next taken in a test tube and heated with a little NaOH solution. A drop of the filtered solution is then added to a freshly prepared solution of sodium nitroprusside taken in a test tube. An intense purple violet colour is developed in solution, which is due to an alkaline sulphide in the drop of the solution added. The sulphide is produced from the sulphate by reduction.

Wet test for sulphate :—An aqueous solution of the sample is taken and to it silver nitrate solution is added. No precipitate is formed, showing the absence of chloride, sulphide, carbonate. To another portion of the aqueous solution of the sample taken in a test tube, a solution of barium chloride is added. A heavy white precipitate, insoluble in HCl, both dilute and concentrated, is produced. Thus, the presence of sulphate as the acid radical in the sample, is confirmed.

(*d*) *Test of sodium :*—There is no wet test for sodium.

Dry test :—A little of the sample is taken on a Pt-wire well cleaned by dipping in conc. HCl and holding in non-luminous Bunsen flame several times till a colourless flame is obtained. The sample is then taken on Pt-wire moistened with conc. HCl and held in the non-luminous Bunsen flame. The flame is coloured golden yellow. The flame coloration completely disappears when viewed through double blue glass. This confirms the presence of sodium.

Dry test for acidic radical, Iodide.—Mixed with manganese dioxide and conc. H_2SO_4 and heated in a test tube, violet vapours of iodine are evolved proving the presence of an iodide.

Wet test for acidic radical, Iodide.—A little of the salt is dissolved in water in a test tube and to it $AgNO_3$ solution is added when a yellow ppt. insoluble in HNO_3 as also in ammonia, is produced. This shows the presence of an iodide.

(*e*) Basic radical—*Lead*—(*i*) *Dry test.*—The substance is mixed with Na_2CO_3 and the mixture is heated on charcoal under the *reducing* blow-pipe flame. A soft metallic bead with lemon-yellow incrustation is obtained. The bead is malleable and marks paper. (*ii*) *Wet test.*—Lead carbonate is insoluble in water and so it is dissolved in dil. HNO_3. The solution is evaporated to dryness and the residue is extracted with water. To the solution dil. HCl is added. White precipitate is obtained. On boiling with water the precipitate dissolves completely and on cooling white crystalline ppt. is again formed. This confirms lead. Further, on adding KI to the hot solution of $PbCl_2$, golden yellow ppt. of PbI_2 is formed. The yellow ppt. of PbI_2 dissolves on boiling with water, and on cooling the solution golden yellow spangles of PbI_2 is obtained, which confirms lead.

Test for carbonate.—On adding dil. HCl to a little of the salt in a test-tube, effervescence occurs. The test-tube is next fitted with a cork through which a bent delivery tube is passed. On adding more salt and more acid, the gas is evolved and passed into lime water. The lime water is turned milky showing the presence of a carbonate.

Q. 5. *20 c. c.'s of a gaseous hydrocarbon are exploded with an excess of oxygen. The contraction observed is 30 c.c. When treated with a solution of KOH, there is a further contraction of 40 c.c.'s. What is the molecular formula of the hydrocarbon ?*

Ans. It can be proved that :

Immediate contraction on explosion = volume of Hydrocarbon taken + the volume of oxygen used up—the volume of carbon dioxide produced.

Here this immediate contraction is given to be 30·0 c.c. and the volume of CO_2 produced is 40 c.c. as observed from KOH-absorption.

$\therefore$ $30 = 20 +$ the volume of oxygen used up $- 40$

$\therefore$ the volume of oxygen used up in the explosion
$= (30 + 40 - 20)$ c.c. $= 50$ c.c.

Now since carbon dioxide contains its own volume of oxygen, 40 c.c. of carbon dioxide must have been formed by taking up 40 c.c. of oxygen. Then, of the 50 c.c. of oxygen used up, 40 c.c. have gone to produce CO_2 and the remaining 10 c.c. have combined with hydrogen of the hydrocarbon. Now 10 c.c. of oxygen can combine with 20 c.c. of hydrogen. That is, the hydrocarbon contains its own volume of hydrogen.

Thus, 1 vol. of hydrocarbon contains 1 vol. of hydrogen. Then, if n be the no. of molecules present in 1 vol. of hydrocarbon,

n mols. of hydrocarbon contain n mols. of hydrogen
[Avogadro's hypothesis]

or, 1 mol. of hydrocarbon contains 1 mol. of hydrogen, *i.e.* 2 atoms of hydrogen (since hydrogen molecules are diatomic)

$\therefore$ the formula for the hydrocarbon may be written as C_xH_2, where x is an integer.

Now to determine x :—

20 c.c. hydrocarbon, on explosion, give 40 c.c. of CO_2

or, 1 vol. of hydrcarbon, on explosion, gives 2 vols. of CO_2.

Let n be the number of molecules present in 1 vol. of the hydrocarbon.

Then n mols. of hydrocarbon, on explosion, give $2n$ mols. of CO_2 [Avogardo's hypothesis],

or, 1 mol. of the hydrocarbon, on explosion, gives 2 mols. of CO_2.

Now 2 molecules of carbon dioxide contain 2 atoms of carbon and these two atoms of carbon must have come from 1 molecule of the hydrocarbon.

Hence $x = 2$, and the formula for the hydrocarbon is C_2H_2.

The hydrocarbon is acetylene, C_2H_2.

1949

FIRST PAPER

Q. 1. *State Gay-Lussac's law of gaseous volumes and Avogadro's hypothesis ; show how they can be related to Daltons atomic theory illustrating your answer by examples.*

Calculate the percentage composition by volume of a mixture of carbon monoxide and methane, 10·5 c.c. of which requires 9 c.c. of oxygen for complete combustion.

Ans. "When gases take part in chemical changes the volumes of the reacting gases and those of the products if gaseous, are in the ratio of small whole numbers, the volumes all being measured under the same condition of temperature and pressure."—This is Gay-Lussac's law of gaseous volumes.

"Equal volumes of all gases and vapours, both elementary and compound, measured under the same conditions of temperature and pressure, contain the same number of molecules"—This is Avogadro's hypothesis.

Gay-Lussac's law of gaseous volumes is based upon experiments. It was thought that Dalton's Atomic theory would provide a simple explanation of the experimental facts discovered by Gay-Lussac. But when Berzelius hazarded a hypothesis in order to correlate Dalton's Atomic theory with Gay-Lussac's Law, viz. "*Equal volumes of all gases under corresponding condition of temperature and pressure contain the same number of atoms,*" [Dalton used the word "atom" for the smallest particle of both elements and compounds, the only difference being made by using the "compound atom" for the ultimate particles of compounds.] his hypothesis failed to supply proper explanation for Gay-Lussac's Law, because it was based upon a false reasoning. The difficulty is seen by applying the above hypothesis to the composition of steam.

Gay-Lussac found by actual experiment that 2 vols. of hydrogen combine with 1 vol. of oxygen to form 2 vols. of steam.

Let "*n*" be the no. of "atoms" present in 1 vol. Since equal volumes of all gases, under similar conditions of temp. and pressure, have the same number of atoms, 2*n* atoms of hydrogen combine with *n* atoms of oxygen to form 2*n* atoms of steam or, 2 atoms of hydrogen combine with 1 atom of oxygen to form 2 atoms of steam.

∴ An atom of steam contains ½ atom of oxygen. But according to Dalton's atomic theory atoms are indivisible and so oxygen atom cannot be supposed to be split up into ½ atom during the production of steam. Hence Berzelius' theory fails.

Avogadro, for the first time, drew up a difference between the ultimate particles of elements which can take part in chemical reaction, and the ultimate particles of both elements and compounds which can exist in the free state, retaining all the properties of those elements and compounds. He called the former "atom" and the latter "molecule". The hopothesis advanced by Avogadro has already been stated. When applied to the composition of steam stated above, if "*n*" be the number of molecules present in one volume, then we have 2*n* molecules of hydrogen combine with *n* molecules of oxygen to produce 2*n* molecules of steam. Hence 2 molecules of hydrogen combine with 1 molecule of oxygen to produce 2 molecules of steam.

Now if we suppose that each molecule of oxygen contains at least 2 atoms of oxygen, which is quite possible, since molecules are not supposed to be indivisible, we get each molecule of steam to be formed with at least one atom of oxygen and Dalton's atomic theory is not violated.

Thus Dalton's atomic theory stands modified in the following way due to the discovery of Gay-Lussac's law of gaseous volumes and Avogadro's hypothesis :—

1. Substances (elementary and compound) are made up of molecules, i.e. ultimate particles capable of separate existence ; and the molecules are composed of indivisible particles called atoms.

2. The molecules of a particular substance are similar to one another and possess the same properties and the same mass, but the molecules of different substances differ in properties as also in mass.

3. The molecules of an element consist of atoms which are

all *alike*, but the molecules of a compound consist of atoms which are *not all alike.*

4. When chemical reaction takes place between two or more substances, the molecules of each substance are first disintegrated into atoms, and then the atoms combine together in definite proportion to produce new molecules of the new substance or substances formed.

Let x c.c. be the volume of carbon monoxide. Then, the volume of methane $=(10{\cdot}5-x)$ c.c.

Now, from the equations—

$$\underset{\text{2 vols.}}{2CO}+\underset{\text{1 vol.}}{O_2}=2CO_2$$

and

$$\underset{\text{1 vol.}}{CH_4}+\underset{\text{2 vols.}}{2O_2}=CO_2+2H_2O$$

we knew that CO requires half its volume of O_2 for complete combustion and CH_4 requires double its volume of oxygen for complete combustion.

Hence x c.c. of CO will require $\frac{x}{2}$ c.c. of O_2 for combustion and $(10{\cdot}5-x)$ c.c. of CH_4 will require $2\times(10{\cdot}5-x)$ or $(21-2x)$ c.c. of O_2 for complete combustion.

Then, by the question, we have

$$\frac{x}{2}+21-2x=9$$

whence $x=8$.

Hence volume of CO in the gas-mixture is 8 c.c. and the volume of methane $=10{\cdot}5-8$, or $2{\cdot}5$ c.c. Hence the composition by volume of gas mixture is

$$CO-\frac{8}{10{\cdot}5}\times100 \text{ or } 76{\cdot}2\ \% \text{ app.}$$

$$CH_4-\frac{2{\cdot}5}{10{\cdot}5}\times100 \text{ or } 23{\cdot}8\ \% \text{ app.}$$

Q. 2. *Describe an experiment to prove that hydrogen sulphide is a compound of hydrogen and sulphur, and that it contains its own volume of hydrogen. How would you prove that its molecular formula is given by* H_2S *?*

An excess of ferrous sulphide was added to 125 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 560 c.c. at 0°C. and 760 mm. Calculate the normality of the acid.

Describe, giving equations, the action of hydrogen sulphide on (a) an aqueous solution of caustic soda, (b) an aqueous solution of lead nitrate.

Ans. *Experiment to prove that hydrogen sulphide is a compound of hydrogen and sulphur* :—A straight eudiometer tube is taken with two Pt-wires sealed near the closed end. The tube is filled with mercury and is inverted over a trough of mercury. A certain volume of sulphuretted hydrogen is collected in the tube by displacement of mercury. The enclosed sulphuretted hydrogen is then subjected to electrical sparking by joining the two Pt-wires to the terminals of an induction coil. A yellow solid is deposited on the inner side of the tube and a certain gas remains inside the tube. That the gas is hydrogen is proved by the fact that it burns in air giving water only and is absorbed by palladium. The yellow solid is taken out on a glass rod and burnt in air when the smell of burning sulphur is recognised, proving thereby that the yellow solid is nothing but sulphur. Thus it is proved that sulphuretted hydrogen is a compound of hydrogen and sulphur.

A thumb-tube is completely filled with mercury and inverted over mercury in a trough. A few c.c. of dry sulphuretted hydrogen is collected in the tube by displacement of mercury. The volume is carefully marked by means of a rubber ring after adjusting the mercury level to the same position inside and outside the tube. A piece of metallic tin is introduced into the

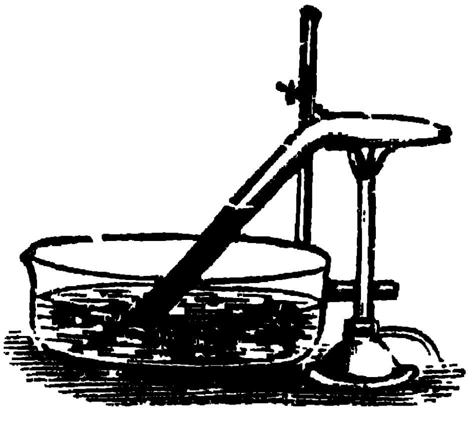


Fig. 60

horizontal part of the tube and it is heated by a burner from outside. Tin combines with sulphur of sulphuretted hydrogen forming tin sulphide and liberating hydrogen. After allowing the tube to cool to the ordinary temperature, the mercury level is adjusted and found to stand at the same level as before. The residual gas is proved to be hydrogen by the facts that it burns with a scarcely visible blue flame with the production of water only and is absorbed by metallic palladium. Hence, the volume of hydrogen liberated is equal to the volume of sulphuretted hydrogen decomposed, or sulphuretted hydrogen contains its own volume of hydrogen.

Then we have, 1 vol. of hydrogen sulphide contains 1 vol. of hydrogen. Let "n" be the number of molecules present in each volume of gas. Therefore n molecules of hydrogen sulphide contain n molecules of hydrogen (Avogadro's hypothesis). Hence, 1 molecule of hydrogen sulphide contains 1 molecule or 2 atoms of hydrogen, since hydrogen molecule is diatomic (Deduction from Avogadro's hypothesis). Thus, the formula for hydrogen sulphide is H_2S_x, where x is an integer. Now since the density of hydrogen sulphide is 17 (Experimental) its molecular weight is $2 \times 17 = 34$ (Deduction from Avogadro's hypothesis).

Now, of the 34 parts by weight of hydrogen sulphide, 2 parts is accounted for by 2 atoms of hydrogen ; the remaining 32 parts are to be accounted for by x atoms of sulphur. Now 32 is the atomic weight of sulphur and it can stand for only one atom of sulphur. Therefore $x = 1$, and the molecular formula for hydrogen sulphide is H_2S.

The sum :—

From the equation

$$\underset{}{FeS} + \underset{98}{H_2SO_4} = FeSO_4 + \underset{34}{H_2S}$$

we know that 34 grams of H_2S can be obtained by the use of 98 grams of sulphuric acid. Now 34 grams of H_2S occupy 22·4 litres at 0°C. and 760 mm. pressure (at N. T. P.) since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P. Therefore 22400 c.c. of H_2S at at 0°C. and 760 mm. can be obtained from 98 grams of sulphuric acid. Hence 560 c. c. of H_2S at 0°C. and 760 mm.

can be obtained from $\frac{98}{22400} \times 560$ gram or $\frac{49}{20}$ grams of H_2SO_4. Thus, in 125 c.c. of dilute sulphuric acid used, are present $\frac{49}{20}$ grams of H_2SO_4. Therefore, in 1000 c.c. of dilute sulphuric acid used, there are present $\frac{49}{20} \times 8$ grams, or $\frac{49 \times 2}{5}$ grams of sulphuric acid.

Now, normal solution of sulphuric acid contains 49 grams of sulphuric acid in 1000 c. c. of the solution.

Hence, the strength of the dilute sulphuric acid used = $\frac{49 \times 2}{5 \times 49} N = \frac{2}{5} N = 0{\cdot}4N$.

(*a*) On passing hydrogen sulphide into an aqueous solution of caustic soda, at first sodium sulphide is formed, but on passing excess of hydrogen sulphide, sodium hydrosulphide results.

$$2NaOH + H_2S = Na_2S + 2H_2O$$
$$NaOH + H_2S = NaHS + H_2O.$$

Both Na_2S and NaHS remain dissolved in water since they are soluble in water.

(*b*) On passing hydrogen sulphide into an aqueous solution of lead nitrate, black lead sulphide is precipitated and nitric acid is formed in solution. On passing hydrogen sulphide further into that solution, sulphur is precipitated along with lead sulphide.

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$$
$$2HNO_3 + H_2S = 2H_2O + 2NO_2 + S.$$

Q. 8. *Describe the preparation of nitric acid. Starting from nitric acid, how would you obtain (a) nitrous oxide, (b) nitric oxide. (c) ammonia ? Give equations.*

State the properties and uses of nitric acid.

Ans. Nitric acid is prepared in the laboratory by heating gently a mixture of equal parts by weight of potassium nitrate and conc. Sulphuric acid, taken in a retort. The stem of the retort enters into a receiver which is kept cool in a stream of cold water. Nitric acid being volatile distils over and collects in the flask.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Nitric acid can also be obtained by the catalytic oxidation of ammonia. A mixture of 1 vol. of ammonia and 7·5 vols. of air, carefully purified, is preheated to 500°C. and is passed through a converter, containing platinum gauzes. The exit gases from the converter, containing NO, NO_2 and steam are cooled and passed into packed stainless steel towers through which water circulates. Formation of nitric acid occurs.

$$\begin{aligned} 4NH_3 + 5O_2 &= 4NO + 6H_2O \\ 2NO + O_2 &= 2NO_2 \\ 3NO_2 + H_2O &= 2HNO_3 + NO. \end{aligned}$$

(*a*) For getting nitrous oxide from nitric acid, dilute nitric acid is allowed to react with zinc in the cold.

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

The gas is to be collected by displacement of warm water.

(*b*) When moderately dilute nitric acid is allowed to react with metallic copper, nitric oxide is evolved.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

At first the brown fumes produced inside the generating apparatus by reactions of NO with oxygen of air is allowed to be swept out and then the gas is collected by displacement of water.

(*c*) When moderately dilute HNO_3 reacts with metallic zinc, ammonium nitrate along with zinc nitrate is formed in solution.

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The solution is next made alkaline with NaOH, excess of NaOH added and the mixture heated to boiling when ammonia is evolved as gas. It can be dried in a lime-tower and collected by downward displacement of air.

$$NH_4NO_3 + NaOH = NaNO_3 + NH_3 + H_2O.$$

Properties and uses of nitric acid :—

Nitric acid is a colourless, fuming liquid with peculiar choking smell. It has a specific gravity of 1·5 and boils at 86°C. with partial decomposition. It is highly corrosive. When it comes in contact with skin, it stains the skin yellow and produces painful wounds. When heated, it decomposes into nitrogen peroxide, oxygen and water,

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

It is a very powerful oxidising agent. A piece of red-hot charcoal burns brilliantly when thrown into concentrated acid ; dry sawdust chars and even burns when conc. nitric acid is poured on it. Sulphur, phosphorus and iodine are oxidised respectively into sulphuric acid, phosphoric acid and iodine by concentrated nitric acid.

$$S + 2HNO_3 = H_2SO_4 + 2NO$$
$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

Ferrous sulphate solution is oxidised to ferric sulphate in presence of sulphuric acid by treatment with nitric acid.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

It bleaches indigo solution. Nitric acid readily dissolves all metals except gold, platinum, and iridium.

Nitric acid is used in the manufacture of sulphuric acid, explosives like nitroglycerine, gun cotton, etc., coal-tar colours and metallic nitrates. It is also used for etching names and designs on copper, brass, bronze, etc. It is also used in setting up certain batteries and in staining feather, wool and silk yellow.

Q. 4. *How would you prepare a pure and dry specimen of carbon monoxide ? Give a neat sketch of the apparatus. Describe the properties of the gas. You are given a mixture of hydrogen and carbon monoxide : how would you separate one of the constituents of the mixture ?*

Ans. Preparation of CO : Conc. H_2SO_4 is taken in a flask fitted with a rubber cork through which pass a dropping funnel and a delivery tube. Sulphuric acid is then heated to about 100°C. and pure formic acid is added drop by drop from the dropping funnel to the hot sulphuric acid. As each drop of formic acid comes in contact with conc. H_2SO_4, the elements of water are abstracted from it and CO gas is evolved. The gas is collected by displacement of water.

$$H.COOH + H_2SO_4 = CO + [H_2SO_4 + H_2O].$$

Pure and dry specimen of the gas can be obtained by passing this CO first through a wash bottle containing concentrated H_2SO_4 and then collecting the gas by displacement of mercury.

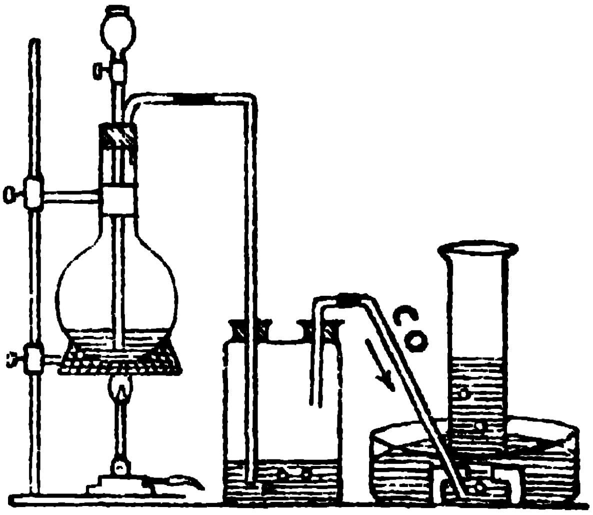


Fig. 61

Properties of carbon monoxide, CO.—

Carbon monoxide is a colourless gas with a peculiar faint smell. It is slightly lighter than air and is practically insoluble in water. The gas is extremely poisonous : it combines with the hæmoglobin of blood forming *carboxy-haemoglobin* which is incapable of absorbing oxygen ; thus blood in the lungs loses its capacity of taking up oxygen and thus brings about insensibility and ultimately death.

Carbon monoxide is a combustible gas. It burns with a characteristic lambent blue flame, forming CO_2, when ignited, $2CO + O_2 = 2CO_2$. An intimate mixture of carbon monoxide and oxygen when inflammed explodes violently.

It is a neutral oxide of carbon. It is an *unsaturated* compound and combines directly with chlorine, under the influence of sunlight, with the formation of carbonyl chloride of *phosgene gas* : $CO + Cl_2 = COCl_2$. Finely divided nickel, cobalt and iron unite with carbon monoxide on heating, with the formation of a class of compounds called *carbonyls*, *e.g.*, nickel carbonyl $Ni(CO)_4$, iron carbonyl, $Fe(CO)_5$ etc.

Carbon monoxide is a powerful reducing agent at an elevated temperature. Thus when carbon monoxide is passed over red-hot copper oxide, CuO is reduced to metallic copper and CO is oxidised to CO_2. $CuO+CO=Cu+CO_2$. Solid KOH, when heated, absorbs CO when passed into it under pressure forming potassium formate; $KOH+CO=HCOOK$. A solution of cuprous chloride in conc. HCl or in ammonia absorbs carbon monoxide, forming $CuCl, CO, 2H_2O$.

Separation of carbon monoxide from hydrogen :—

Carbon monoxide can be removed by passing the mixture of carbon monoxide and hydrogen through an ammoniacal solution of cuprous chloride, which absorbs carbon monoxide, and hydroden will escape as gas. Hydrogen is dried by passing through a wash bottle containing conc. H_2SO_4 and then collected, free from carbon monoxide, by displacement of mercury.

Industrially the separation is effected in the following way :

The mixture of carbon monoxide and hydrogen is mixed with steam and passed over a catalyst consisting of ferric oxide, with promoter like chromic oxide heated to a temperature of 450° – 550°C. The carbon monoxide reacts with steam, producing carbon dioxide and hydrogen :

$$CO+H_2O=CO_2+H_2.$$

The carbon dioxide is then removed by washing with water at 25 atmospheres pressure and the remaining trace of carbon monoxide is removed by washing the gas, under 200 atmospheres pressure, with ammoniacal cuprous formate solution and then with 25 per cent. caustic soda solution at 260°C., in steel towers.

$$\underset{\text{Sodium formate.}}{CO+NaOH=HCOONa.}$$

Q. 5. *Compare the physical and chemical properties of the main allotropic modifications of phosphorus. Describe experiment to prove that they are different forms of one and the same element. How is phosphorus prepared from calcium phosphate? State the uses of phosphorus.*

Ans. The main allotropic modifications of phosphorus are white phosphorus and red phosphorus.

Comparison of properties of white and red Phosphorus :—

Property	White P	Red P
1. Colour.	Almost colourless.	Chocolate red.
2. Smell.	Garlic odour	Odourless.
3. Specific gravity.	1·83	2·05—2·39
4. Melting point.	44°C.	500°—600°C.
5. Action of CS_2, chloroform etc.	Readily soluble	Insoluble.
6. Reaction when exposed to air.	Phosphoresces with glow and oxidation.	Does not phosphoresce (there is no glow and no oxidation).
7. Ignition temp.	30°C.	240°C.
8. Hot NaOH sol.	Readily reacts with NaOH sol. when heated, giving off phosphine.	No action.
9. Chemical activity.	Highly active.	Less active than yellow P.
10. Physiological action.	Highly poisonous.	Not poisonous.

Experiments to prove that white P and red P are different forms of one and the same element :—

(1) Equal weights of white P and red P are taken and burnt carefully in excess of oxygen by suitable arrangement so that

there is no loss of the products formed in each case. The products are collected separately and dissolved in excess of water, whereby phosphoric acid, H_3PO_4, is formed in both the cases. The two different solutions so obtained are neutralised with ammonia and completely precipitated separately with magnesia mixture in presence of ammonia and ammonium chloride. The precipitates are filtered, washed and ignited and weighed. Heating, cooling in a desiccator and weighing are carried out till the weights in the two cases become constant.

It will be found, if the experiment be carefully performed, that the weights of magnesium pyrophosphate so obtained in the two cases are the same, proving thereby that we are dealing with one and the same element.

(2) When red phosphorus is heated in an inert atmosphere above 550°C. so that vapours are produced and the vapours are rapidly cooled, white P is obtained. Again, if white P is heated to 240°C. in an inert atmosphere with a trace of iodine (catalyst), red P is formed. This interconvertibility shows that white P and red P are allotropic modifications of the same element.

Preparation of phosphorus from Calcium phosphate :—

A charge of powdered calcium phosphate, sand and coke is fed through the hopper of a furnace, which is shown diagrammatically in the adjoining figure, by means of a *warm-conveyer*

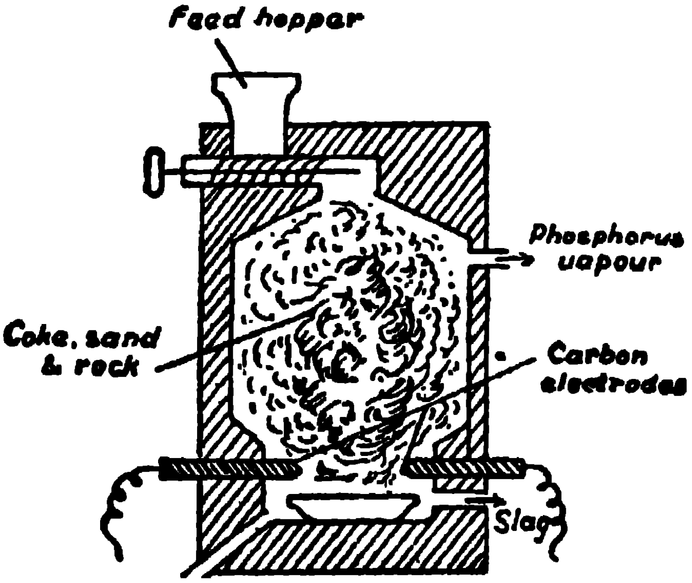


Fig. 62

which pushes it on into the furnace. A powerful electric arc is then struck between the two carbon rods, set a little above the bottom of the furnace. By this means the mixture is heated to a temperature of about 1200°—1300°C. when the different substances react and phosphorus is produced as vapour along with carbon monoxide gas. These gaseous products pass out by means of the exit near the top and are bubbled through water contained in a tank. Phosphorus vapour condenses to the solid state under water and carbon monoxide escapes as gas. The residue of fused calcium silicate present in the furnace is taken out by means of the slag hole at the bottom of the furnace. The process is continuous and more charge is continuously added through the hopper. The reactions that take place in the furnace may be represented by the following equations :—

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5C = 2P + 5CO$$

Uses of phosphorus :—

(1) Phosphorus is chiefly used in making matches. White phosphorus was at one time used for making "strike-any-where" "Lucifer" matches, but its use in that way is now prohibited by law. Red phosphorus is now employed for making the "safety" matches. Scarlet phosphorus and phosphorus sulphide, P_2S_3 are now employed instead of white phosphorus in manufacturing matches.

(2) Phosphorus is used as a poison for rats.

(3) A certain amount is used in making phosphor bronzes which are the alloys of copper, tin and phosphorus.

(4) It has also been employed in making incendiary bombs and smoke screens for it burns spontaneously and gives dense white fumes.

(5) Red phosphorus is also used in the laboratory for the preparation of hydrobromic and hydriodic acids. Phosphorus trichloride and phosphorus penta-chloride are made from yellow phosphorus. These two chlorides of phosphorus find wide application. Hypophosphites are manufactured from phosphorus and are employed medicinally.

Q. 6. *Describe the ammonia-soda process for the manufacture of sodium carbonate. What is the difference between sodium car-*

bonate and sodium bicarbonate? Why do their solutions react alkaline? What happens when they are heated? How is sodium carbonate converted into caustic soda? Compare their properties.

Ans. The modern method for the manufacture of sodium carbonate from common salt is the ammonia-soda process or Solvay process. This is based on the reaction between sodium chloride solution and ammonium bicarbonate solution with the precipitation of sodium bicarbonate :—

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

The precipitated sodium bicarbonate is filtered and then heated to give sodium carbonate :—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The working of the process will be clear by reference to the adjoining figure, which gives a diagrammatic representation of the plant used.

The working of the process is as follows :—

(*a*) A strong solution of sodium chloride (brine) is obtained directly from salt-beds by pumping in water into the salt-beds and then pumping out the brine so produced into a brine reservoir (shown on the top left). Brine from that reservoir is next admitted into the saturating tank, which is an upright cylinder. Here the brine is saturated with ammonia. The salts of calcium and magnesium contained in the brine are precipitated by carbon dioxide, coming along with ammonia from the ammonia recovery plant :—

$$\begin{aligned}&2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3\\&CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + CaCO_3\\&MgCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + MgCO_3.\end{aligned}$$

The brine, when fully saturated with ammonia, is run into a settling tank, where the precipitated calcium and magnesium carbonates settle down.

(*b*) Ammoniacal brine is then pumped up from the settling tank to the top of the carbonating tower, provided with perforated horizontal partitions and cooling coils and is made to trickle down the tower. Carbon dioxide gas is admitted at the bottom of the tower, so that carbonation is carried out on the principle of counter currents. Carbon dioxide rises in small

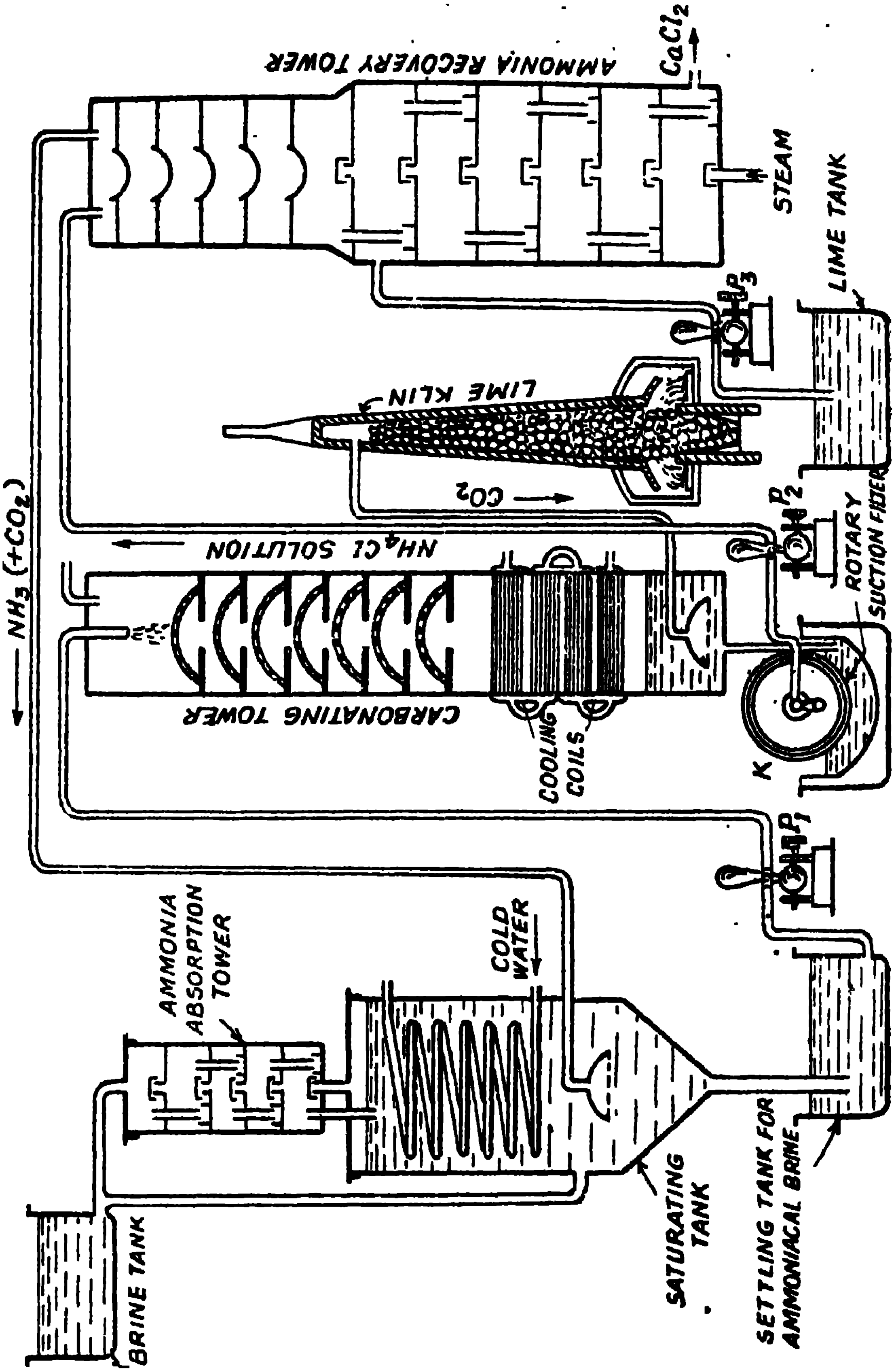


Fig. 63

bubbles through the perforations. The ammonium bicarbonate formed by the interaction of carbon dioxide, ammonia and water, reacts with sodium chloride solution, precipitating sodium bicarbonate :—

$$NH_3 + H_2O + CO_2 = NH_4HCO$$
$$NaCl + NH_4HCO_3 = NaHCO_{33} + NH_4Cl.$$

The milky liquid containing small crytals of sodium bicarbonate is drawn off at the base of the tower and filtered at the rotary vacuum filter. The crystals of sodium bicarbonate are deposited as a layer on the outside of the filter and are collected by scraping with a knife-blade. The mother liquor containing ammonium chloride and some ammonium bicarbonate is pumped to the top of the ammonia recovery tower.

The sodium bicarbonate is next calcined in a covered pan or a rotary furnace fired on the outside. Sodium carbonate is formed and carbon dioxide and steam escape as gas :—

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide evolved here is utilised in the carbonating tower together with the gas from the lime-kiln.

(*c*) In lime-kiln limestone is heated strongly to give carbon dioxide and calcium oxide (quicklime) :—

$$CaCO_3 = CaO + CO_2.$$

The carbon dioxide is led to the carbonating tower, while the quicklime is slaked with a large quantity of water and pumped on to the ammonia recovery plant in the form of milk of lime.

(*d*) In the ammonia-recovery tower, which consists of an upper and a lower part, the mother liquor is fed into the top of the upper part and at the top of the lower part milk of lime is admitted. A current of steam is next admitted at the base of the tower. Ammonium bicarbonate is decomposed by steam, and ammonium chloride is decomposed by lime :—

$$NH_4HCO_3 = NH_3 + H_2O + CO_2$$
$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

The mixture of ammonia with the small amount of carbon dioxide passes on to the saturating tank.

Thus the process is self-sufficient, but certain amount (about 2%) of ammonia is lost during working and is to be replaced.

Sodium carbonate, Na_2CO_3, is a normal salt of hypothetical carbonic acid, H_2CO_3, both the replaceable hydrogen atoms of the acid being replaced by metal sodium. Sodium bicarbonate, $NaHCO_3$, is an acid salt of the same hypothetical carbonic acid, H_2CO_3, because only one atom of replaceable hydrogen is replaced by metallic sodium and the other hydrogen atom being left as such.

Sodium carbonate, Na_2CO_3, and sodium bicarbonate, $NaHCO_3$, react alkaline in water solution, because by *hydrolysis* (decomposition by water) caustic soda and carbonic acid (hypothetical) are produced in solution. Caustic soda is a very strong base in comparison to carbonic acid which is a very weak acid, since it is capable of turning blue litmus only port-wine red. So the alkaline reaction predominates.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$
$$NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3.$$

When sodium carbonate is heated strongly, it fuses but does not undergo any decomposition. But when sodium bicarbonate is heated, it decomposes into sodium carbonate, carbon dioxide, which escapes as gas, and water, which escapes as steam.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Sodium carbonate in water solution is run into *causticisers*, *i.e.*, iron tanks provided with mechanical agitators and fitted with a pipe for admission of steam. Quicklime placed in an iron cage is kept dipping into the top of the solution, the stirrer is worked and steam is passed in. Sodium carbonate then reacts with calcium hydroxide formed and is practically completely converted into caustic soda.

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + \underset{\text{pptd.}}{CaCO_3}$$

The precipitated calcium carbonate is filtered off and caustic soda solution so obtained is evaporated in iron pans to get solid caustic soda.

Sodium carbonate is a weak base, whereas caustic soda is a very strong base. Sodium carbonate reacts with acids with effervescence due to escape of carbon dioxide, whereas caustic soda does not react with acids in that way.

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Actually sodium carbonate is a salt of carbonic acid (hypothetical) and its alkaline reaction is due to hydrolytic decomposition whereas caustic soda is a true base and an alkali.

Q. 7. *Name the important ores of aluminium with their formulæ. How is metallic aluminium obtained? Name the important alloys of aluminium with their constituents.*

Describe the action of a solution of caustic soda and copper sulphate respectively on powdered aluminium.

Ans. The important ores of aluminium are :—

(1) Bauxite, $Al_2O_3, 2H_2O$

(2) Cryolite, $AlF_3, 3NaF$.

There are many naturally occurring compounds of aluminium, viz., felspar ($KAlSi_3O_8$), china clay (Kaolin, $Al_2O_3, 2SiO_2, 2H_2O$), diaspore (Al_2O_3, H_2O). But none of them can be considered as an ore of aluminium, for none can be used for extracting the metal profitably and economically.

The extraction of aluminium is carried out from bauxite. Since bauxite contains impurities like ferric oxide, silica, etc., it is to be purified before being used in the extraction of aluminium. The purification of bauxite can be carried out by

(*a*) **Hall's process**, in which the ore is heated to bright redness with sodium carbonate, when sodium meta-aluminate $NaAlO_2$, is formed. The mass is cooled and rapidly lixiviated with water, whereby sodium meta-aluminate passes into solution and ferric oxide is left as a residue in a finely divided state.

$$Al_2O_3,2H_2O + Na_2CO_3 = 2NaAlO_2 + CO_2 + 2H_2O.$$

The solution of sodium meta-aluminate is removed by decantation, heated to 50° – 60°C. and a current of carbon dioxide is passed through it when hydrated alumina separates out :

$$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3.$$

The precipitated $Al(OH)_3$ is separated, washed, dried and ignited when pure Al_2O_3 is obtained :

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

(*b*) **Baeyer's process**, in which the powdered bauxite is first calcined and the calcined mass is digested in an autoclave at 80 lb. pressure and at 150°C. with caustic soda solution for some hours. Alumina present in the bauxite dissolves with the formation of sodium aluminate and oxide of iron is left behind.

$$Al_2O_3, 2H_2O + 2NaOH = 2NaAlO_2 + 3H_2O.$$

The solution is diluted and filtered and the filtrate agaitated with some freshly precipitated Al$(OH)_3$. Sodium meta-aluminate present in solution is hydrolysed and changes to Al$(OH)_3$.

$$NaAlO_2 + 2H_2O = NaOH + Al(OH)_3.$$

Most of the aluminium present in solution is thus precipitated as Al$(OH)_3$. Precipitated Al$(OH)_3$ is filtered, washed, dried and ignited.

$$2Al(OH)_3 = Al_3O_3 + 3H_2O.$$

The filtrate containing caustic soda is con-centrated and used over again.

(*c*) **Serpek's process**, which is especially suitable for white bauxite containing silica in excess as impurity, consists in heating the ore mixed with carbon at about 1800°C. and passing nitrogen gas over the mixture. Aluminium nitride is formed :

$$Al_2O_3, 2H_2O + 3C + N_2 = 2AlN + 3CO + 2H_2O.$$

This aluminium nitride is next hydrolysed by water, when Al$(OH)_3$ is formed :

$$2AlN + 6H_2O = 2Al(OH)_3 + 2NH_3.$$

The residue of Al$(OH)_3$ is ignited to give Al_2O_3.

Purified alumina obtained by operating any of the above processes is next dissolved in fused cryolite and electrolysed between carbon electrodes. Electrolysis is carried out in an iron box lined inside with gas carbon. This serves as the cathode.

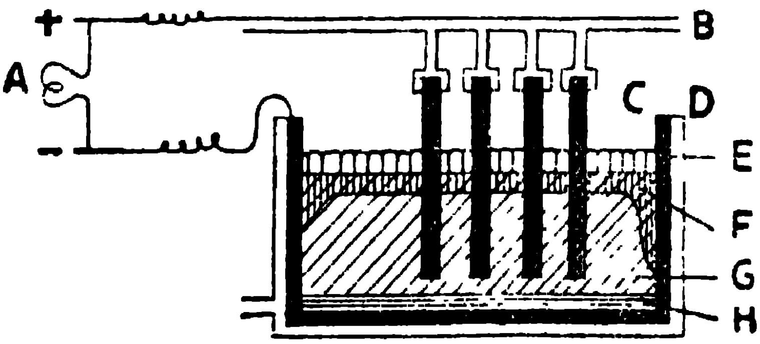


Fig. 64

The anode consists of a number of vertical carbon rods reaching nearly the gas carbon base and suspended from a copper rod at the top. The electrolyte is pure alumina dissolved in fused cryolite (Na_3AlF_6) and maintained at a temperature of 900°—950°C. by the heat produced as a result of the passage of the current. The charge is covered by a layer of solid crust due to cooling and above that solid crust a layer of powdered anthracite is spread out in order to prevent the blinding glow of the bath from reaching the eye.

When the current is passed, alumina undergoes decomposition :

$$2Al_2O_3 = 4Al + 3O_2.$$

Molten aluminium sinks to the bottom of the bath below the anodes. The oxygen liberated at the anodes oxidises the anode material with the production of CO and CO_2. Aluminium is tapped off from time to time through the tapping hole near the base. When the alumina is used up, the resistance of the bath increases and thereby a lamp shunted off the circuit begins to glow. Workmen then understand that fresh charge is to be added. The process is thus made continuous.

Important alloys of aluminium are :—

(1) Magnalium—alloys of aluminium and magnesium.

(2) Duralumin—alloy of aluminium, magnesium, copper and manganese.

(3) Aluminium bronzes—alloys of aluminium and copper.

When powdered aluminium is heated with a solution of caustic soda, aluminium dissolves as sodium aluminate and hydrogen is evolved.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

When powdered aluminium is added to copper sulphate solution, metallic copper is deposited and aluminium passes into solution as aluminium sulphate.

$$3CuSO_4 + 2Al = 3Cu + Al_2(SO_4)_3.$$

Q. 8. *Explain briefly, giving equations, what happens when (a) a hot solution of ferric chloride in hydrochloric acid is treated with a solution of stannous chloride ; (b) a solution of mercuric chloride in presence of hydrochloric acid is treated gradually with solution of stannous chloride ; (c) chlorine is passed into a strong solution of caustic potash ; (d) mercury is ground up with* *sulphur* ; (*e*) *a solution of caustic soda is gradually added to that of zinc sulphate.*

Ans. (*a*) When a hot solution of ferric chloride in hydrochloric acid, which is reddish yellow in colour, is treated with a solution of stannous chloride, ferric chloride is reduced to ferrous chloride and the solution becomes colourless. Stannous chloride is oxidised to stannic chloride and remains in solution.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

(*b*) When a solution of mercuric chloride in presence of hydrochloric acid is treated gradually with a solution of stannous chloride, at first a white precipitate of mercurous chloride, produced by the reduction of mercuric chloride, is formed. Stannic chloride is also produced in solution from the oxidation of stannous chloride. On further addition of stannous chloride, a grey precipitate of metallic mercury results from the reduction of mercurous chloride formed and further quantity of stannic chloride is produced in solution from the oxidation of stannous chloride.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

(*c*) When chlorine is passed into a strong solution of caustic potash, so long as the solution is alkaline, potassium hypochlorite, and potassium chloride are formed along with water, but when the solution gets hot due to reaction proceeding and the chlorine is passed nearly to saturation, potassium chlorate, which separates as crystals, is formed, along with potassium chloride and water.

$$2KOH + Cl_2 = KOCl + KCl + H_2O \text{ (alkaline)}$$
$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O \text{ (excess of chlorine).}$$

(*d*) When mercury is ground up with sulphur, mercuric sulphide is formed. It is black in colour, but on heating it turns red. $Hg + S = HgS$.

(*e*) At first a white precipitate of zinc hydroxide is formed :

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4.$$

On adding further quantity of caustic soda solution after complete precipitation of $Zn(OH)_2$, the precipitate dissolves with the formation of sodium zincate :—

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

SECOND PAPER—1949

Q. 1. *State and explain the law of multiple proportions.*

1·00 gm. of copper was dissolved in nitric acid and on ignition gave 1·25 gm. of cupric oxide. 1·00 gm. of cuprous oxide when ignited in a current of hydrogen gave 0·888 gm. of copper.

Show that these results illustrate the law of multiple proportions and calculate the percentage of copper in each oxide.

Ans. Law of Multiple Proportions :—

When one element combines with a second element to form two or more different compounds, the different weights of one of the elements, which combine with a constant weight of the other, bear a simple ratio to one another.

The expression *simple ratio* means that the ratio can be expressed by small whole numbers not exceeding five.

The law will be clearly understood by studying certain examples.

(1) Hydrogen combines with oxygen to form two different compounds, viz., water and hydrogen peroxide. In water 1 part by weight of hydrogen has combined with 8 parts by weight of oxygen. In hydrogen peroxide, 1 part by weight of hydrogen has combined with 16 parts by weight of oxygen.

Thus, the different weights of oxygen (viz. 8 and 16) which combine, in these two cases, with the same weight of hydrogen (viz. 1) bear to each other the ratio 8 : 16 or 1 : 2.

(2) Nitrogen and oxygen combine together to form five different oxides. On analysis, they show that—

In *nitrous oxide*, 14 parts by weight of nitrogen has combined with 8 parts by weight of oxygen.

In *nitric oxide*, 14 parts by weight of nitrogen has combined with 16 parts by weight of oxygen.

In *nitrogen trioxide*, 14 parts by weight of nitrogen has combined with 24 parts by weight of oxygen.

In *nitrogen peroxide*, 14 parts by weight of nitrogen has combined with 32 parts by weight of oxygen.

In *nitrogen pentoxide*, 14 parts by weight of nitrogen has combined with 40 parts by weight of oxygen.

Thus the different weights of oxygen (viz., 8, 16, 24, 32, 40) which combine with a fixed weight of nitrogen (viz. 14) bear to to one another the ratio 8 : 16 : 24 : 32 : 40 or 1 : 2 : 3 : 4 : 5, a a simple proportionality being readily seen.

In cupric oxide, from the given data, 0·25 gm. of oxygen has combined with 1·00 gm. of copper. Therefore, 1 gm. of oxygen is in combination with 4 gms. of copper in cupric oxide.

In cuprous oxide, from the given data, 0·112 gm. of oxygen has combined with 0·888 gm. of copper. Therefore, 1 gm. of oxygen is in combination with $\frac{0{\cdot}888}{0{\cdot}112}$ gm. or 8 gms. (nearly) of copper. Hence the amounts of copper which have gone to combine with a constant weight, *viz.* 1 gm. of oxygen to form cupric and cuprous oxides respectively are in the ratio of 4 : 8, *i. e.* 1 : 2 which is a simple ratio. Thus the results given illustrate the law of multiple proportions.

In cupric oxide, 1·25 gm. of the oxide contain 1 gm. of copper. Therefore, percentage of copper in cupric oxide

$$=\frac{1}{1{\cdot}25}\times 100=80.$$

In cuprous oxide, 1 gm. of the oxide contains 0·888 gm. of copper. Therefore percentage of copper in cuprous oxide

$$=\frac{0{\cdot}888}{1}\times 100=88{\cdot}8.$$

Q. 2. *Give an account of the preparation of fluorine, describing carefully the apparatus used. State its properties.*

Can fluorine be prepared by the electrolysis of an aqueous solution of a fluoride ? Give reasons for your answer.

Ans. Fluorine is now-a-days prepared by electrolysing fused potassium hydrogen fluoride, KHF_2 (**Fremy's salt**). The apparatus consists of V-tube made of copper which is provided with two side tubes. The copper V-tube is fitted with bakelite stoppers, and two *graphite* electrodes are introduced through these bakelite stoppers. Potassium hydrogen fluoride is placed in the tube which is heated electrically by coils wound round the outside of the tube. Electric current is next passed through the fused KHF_2 when decomposition occurs and fluorine is liberated at the anode and hydrogen at the cathode. The gas evolved at the anode comes out of the side-tube and is next passed through a number of U-tubes, also made of copper, containing *dry* sodium fluoride which absorbes HF vapour coming out along with fluorine. The gas is then collected in a vessel by the displacement of air.

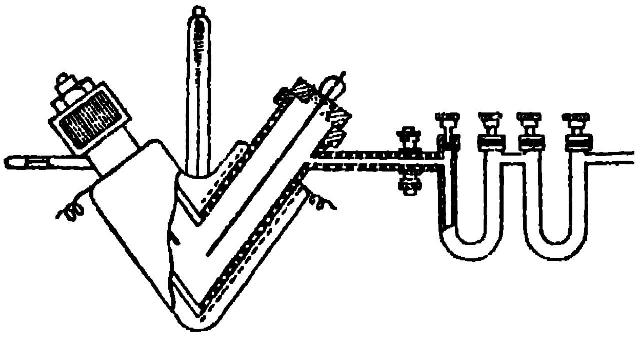


Fig. 65

KF undergoes electrolysis with the liberation of potassium at the cathode and fluorine at the anode. Then secondary reaction takes place at the cathode, and the liberated potassium reacts with HF present in the electrolyte with production of KF and liberation of hydrogen which is evolved as gas at the cathode

$$KF \rightarrow K \text{ (at the cathode)} + F \text{ (at the anode)}$$

$$\left.\begin{array}{l}\text{At the}\\ \text{cathode}\end{array}\right\} \begin{array}{l}K+HF=KF+H\\ H+H=H_2.\end{array} \qquad \begin{array}{l}\text{At the}\\ \text{anode}\end{array} \quad F+F=F_2.$$

Properties of fluorine :—Fluorine is a pale greenish yellow gas with a peculiar penetrating smell. It attacks the mucous membranes. It is heavier than air, Its solubility in water is not known beceuse it readily reacts with water, evolving ozonised oxygen,

$$2F_2+2H_2O=4HF+O_2$$
$$3F_2+3H_2O=6HF+O_3$$

Fluorine is one of the most chemically active elements. It reacts with nearly all elements except nitrogen, helium and argon. It fumes in moist air, forming hydrogen fluoride with the hydrogen present in water vapour found in air. In *dry* air fluorine does not fume.

Fluorine combines with all metals. Na, K, Ca etc. are attacked at once ; Ag, Al, Ni, Fe, Zn, Sn, Mg catch fire and burn in fluorine when gently warmed ; Au, Pt, etc. are not attacked by fluorine at the ordinary temperature but form fluorides on heating. Cu is coated with a superficial layer of its fluoride, on being exposed to fluorine and further action of fluorine stops. Finely divided metals, when introduced into fluorine gas, burn spontaneously. Non-metals like boron (amorphous), carbon (charcoal and lamp-black), silicon (crystalline), sulphur, phosphorus, bromine, iodine, etc. all spontaneously catch fire and burn in fluorine gas. Arsenic and antimony, when introduced into fluorine, spontaneously catch fire and burn, giving their fluorides. When fluorine is passed into 2% solution of caustic soda, sodium fluoride is formed in solution and fluorine monoxide (F_2O) is evolved as gas :

$$2NaOH + 2F_2 = 2NaF + F_2O + H_2O.$$

When passed into strong caustic soda solution, fluorine liberates oxygen as gas and NaF is formed in solution.

Fluorine cannot be prepared by the electrolysis of an aqueous solution of a fluoride, say sodium fluoride. This is because of the fact that fluorine is a very active element and it has a very great affinity for hydrogen. Supposing during electrolysis of a solution of a fluoride, fluorine is liberated at the anode, that fluorine will attack water present there and hydro-fluoric acid will be formed and oxygen will be liberated, which will evolve as gas. Sodium liberated at the cathode will also react with water forming sodium hydroxide and liberating hydrogen, which will evolve also as gas, Sodium hydroxide formed at the cathode will react with hydrofluoric acid formed at the anode forming original sodium fluoride and water. So the net result of electrolysis of a solution of sodium fluoride is the same as the electrolysis of water with evolution of hydrogen at the cathode and oxygen at the anode.

$$NaF \rightleftharpoons Na^+ + F^-$$

$$F^- + F^- \rightleftharpoons F_2 + 2e \text{ (at the anode)}$$

$$2F_2 + 2H_2O = 4HF + O_2 \text{ (at the anode)}$$

$$2Na + 2H_2O = 2NaOH + H_2 \text{ (at the cathode)}$$

$$NaOH + HF = NaF + H_2O.$$

Q. 3. *You are given a mixture containing three parts by volume of carbon monoxide and one part by volume of carbon dioxide. How would you convert the mixture completely into :—*

(*a*) *carbon monoxide* ; (*b*) *carbon dioxide ?*

State the changes of volume, if any, in each case.

Ans. (*a*) The mixture is passed through an iron tube packed with charcoal which is heated to a red heat in a furnace.

Carbon dioxide present in the mixture will be reduced completely to carbon monoxide by this operation.

$$\begin{array}{ccc} CO_2 + C & = & 2CO \\ \text{1 vol.} & & \text{2 vols.} \end{array}$$

From the above equation we know that 1 vol. of carbon dioxide gives rise to 2 vols. of carbon monoxide. So the final volume of 4 vols. of the gas mixture will be 3 vols. of CO + 2 vols. of CO resulting from 1 vol. of CO_2, *i.e.*, the result will be 5 vols. of CO. Hence there will be an increase in volume by ¼th of the total volume taken.

(*b*) The mixture is passed through a hard-glass tube containing cupric oxide heated to redness. Carbon monoxide will thereby be completely converted into carbon dioxide.

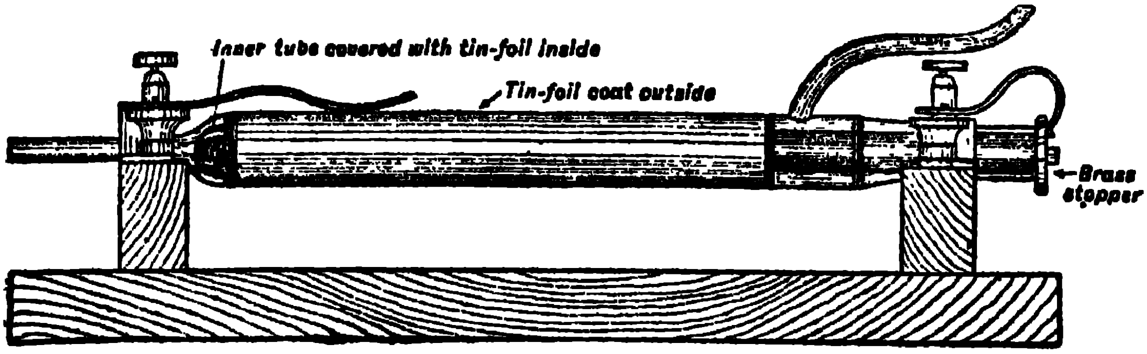
$$\begin{array}{ccccc} CO & + & CuO & = & CO_2 + Cu \\ \text{1 vol.} & & & & \text{1 vol.} \end{array}$$

From the above equation we know that 1 vol. of carbon monoxide produces 1 vol. of carbon dioxide. Thus, 3 vols. of CO will give rise to 3 vols. of CO_2. Hence in the second case 4 vols. of the gas mixture will remain as such, and there will be no change of volume.

Q. 4. *How is ozone prepared ? State its properties, tests and uses.*

How would you distinguish ozone from hydrogen peroxide ?

Ans. Ozone is prepared by subjecting pure, dry oxygen to the action of silent electric discharge in Siemen's ozoniser which consists of two co-axial glass tubes hermetically sealed. The



Siemens' ozoniser.

Fig. 66

outer tube of the ozoniser is coated on the outside and the inner tube on the inner side with tin-foils. These tin-foils are connected to the two binding screws which, in their turn, are in connection with a Ruhmkorff's induction coil. Dry oxygen is passed through the annular space in slow stream and a series of silent electric discharge is passed. The gas coming out of the exit tube consists of a mixture of ozone and oxygen.

$$3O_2 = 2O_3.$$

The conversion of oxygen into ozone is only to the extent of 5 to 6%.

Properties. *Physical.*—It is a pale blue gas with a fishy odour. It is slightly soluble in water, but readily dissolves in essential oils like oil of cinnamon or oil of turpentine. It is unstable and decomposes when heated to about 250°—300°C., being reconverted into oxygen.

Chemical.—It is a powerful oxidising agent. It oxidises S, P and As to their highest oxyacids.

$$S + H_2O + 3O_3 = H_2SO_4 + 3O_2.$$

It liberates halogens from their hydracids :

$$2HCl + O_3 = Cl_2 + H_2O + O_2.$$

It also liberates iodine from neutral potassium iodide :

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2.$$

It oxidises moist I_2 to HIO_3 ;

$$I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2.$$

Lead sulphide is oxidised by ozone readily to lead sulphate, the colour changing thereby from black to white ;

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

In all these oxidation reactions, an equivalent amount of oxygen is set free. But in the oxidation of SO_2 to SO_3 and of $SnCl_2$ in HCl solution to $SnCl_4$, ozone is completely absorbed :

$$3SO_2 + O_3 = 3SO_3.$$
$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O.$$

Ozone oxidises mercury to Hg_2O ; a drop of mercury exposed to ozone loses its mobility and sticks to glass. It bleaches vegetable colours by oxidation. Ozone is catalytically decomposed by oxides of silver, iron, cobalt, etc. and by shaking it with powdered glass, Even metallic Ag, Pt and Pd decompose ozone catalytically.

Tests.—Ozone is recognised by its strong, characteristic fishy odour. It liberates iodine from potassium iodide and so can be tested for with iodised starch paper which turns blue by the action of ozone. But this is not a specific test for ozone, since other .oxidizing agents like hydrogen peroxide or chlorine or oxides of nitrogen will do the same. A paper soaked in an alcoholic solution of *tetramethyl base* is turned *violet* by ozone. This is a specific reaction for ozone and detection can be carried out with its help. Similarly, a piece of paper soaked in a solution of *benzidine* is turned *brown* by ozone.

Uses of ozone :—(1) The chief use of ozone is for sterilizing water. The drinking water supply is fitted with an ozoniser and the water is sterilised by treatment with ozone.

(2) Ozone is used in underground tube railways for keeping the air fresh. Also the air inside crowded rooms is purified and rendered invigorating by injecting ozonised oxygen in those rooms by fan arrangements.

(3) Ozone is also used for bleaching oils, flour, starch, etc.

(4) Ozone is now employed in synthetic perfume industry in oxidising iso-eugenol to vaniline, the parent substance of synthetic perfumes. It is also used in oxidising potassium manganate to potassium permanganate.

Distinguishing Tests for Ozone and Hydrogen Peroxide :—

Ozone	*Hydrogen peroxide*
1. Ozone is a gas	1. Hydrogen peroxide is a syrupy liquid.
2. It has a fishy odour.	2. It is colourless.
3. It cannot liberate iodine from potassium iodide solution in presence of ferrous sulphate.	3. It liberates iodine from KI sol. even in presence of $FeSO_4$.

Ozone	*Hydrogen peroxide*
4. It gives no colour reaction with	4. It gives
(*a*) $K_2Cr_2O_7$ sol. acidified with H_2SO_4.	(*a*) Azure-blue coloration with $K_2Cr_2O_7$ sol. + H_2SO_4, the colour being extracted with ether when shaken with it ;
(*b*) Titanicum salt solution.	(*b*) Orange coloration with titanium salt solution.
5. It cannot decolorise acidified $KMnO_4$ solution.	5. It readily decolorises acidified $KMnO_4$ solution.
6. Ozone turns paper soaked in an alcoholic solution of tetramethyl base purple violet.	6. H_2O_2 has. no action on tetramethyl base paper.

Q. 5. *How would you prove that carbon is a constituent of chalk, nitrogen is a constituent of nitre, copper is a constituent of blue vitriol and mercury is a constituent of calomel ?*

Ans. Chalk is calcium carbonate. On heating chalk in a hard-glass test tube a gas is evolved, which is collected in a gas jar by displacement of mercury. Then a piece of burning magnesium ribbon is introduced into the gas-jar. Magnesium ribbon continues to burn, producing a white deposit with black specks. Dilute hydrochloric acid is next added to the gas-jar, when the white deposit dissolves, leaving the black particles which float upon the solution. These black particles are collected, dried, and then burnt in oxygen gas taken in another gas jar. Lime-water is then added to the gas-jar in which these black particles are burnt. Lime water turns milky, showing the presence of carbon dioxide in the jar. This carbon dioxide must have been produced by the burning of the black particles, which are, therefore, nothing but carbon. This carbon has come from the gas obtained by heating chalk, for magnesium ribbon does not contain any carbon. Hence chalk contains carbon.

Nitre is potassium nitrate. To show that nitrogen is a constituent of nitre, nitre is taken in a hard glass test tube fitted with a cork through which passes a delivery tube. The hard glass test tube is fitted to a clamp in an inclined position and the delivery tube is dipped under water contained in a pneumatic trough over which a gas jar containing water is inverted. The hard glass test tube is heated till the nitre fuses. Then a bit of sulphur is introduced by opening the cork and the cork is immediately replaced. A gas is evolved, which collects inside the jar by displacement of water. That the gas collecting is nitrogen can be proved by the facts that it is inert, it does not support combustion and does not turn lime-water milky and is absorbed by heated magnesium. This gas comes from nitre since sulphur does not contain any nitrogen. Thus nitre is proved to contain nitrogen.

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

To show that copper is a constituent of blue vitriol, a solution of blue vitriol is taken in a basin and aluminium powder is added to it. Aluminium powder passes into solution and red metallic copper is deposited. This copper comes from blue vitriol, since aluminium powder does not contain any copper. This experiment proves that copper is a constituent of blue vitriol.

$$3CuSO_4 + 2Al = Al_2(SO_4)_3 + 3Cu.$$

To show that mercury is a constituent of calomel, *i.e.*, mercurous chloride, mercurous chloride is mixed thoroughly with soda-lime and the mixture taken in a hard glass test tube and heated. Small globules of mercury are found to be deposited in the upper cooler part of the test tube forming a shining mirror. These small globules are scratched with a glass rod and poured on a piece of paper when a bigger globule of mercury is obtained. This mercury certainly comes from calomel and not from soda-lime, which does not contain any mercury. Thus, it is proved that mercury is a constituent of calomel or mercurous chloride.

$$2Hg_2Cl_2 + 4NaOH = 4Hg + 4NaCl + 2H_2O + O_2.$$

Q. 6. *Explain and illustrate what you understand by the following :—*

(a) Basic salt ; (b) Dialysis ; (c) Dissociation ; (d) Catalytic agent ; (e) Electro-chemical equivalent.

Ans. (*a*) Basic salts are those salts produced by the interaction of acids with poly-acidic bases in such a fashion that partial replacement of the hydroxyl groups of the bases has taken place by the acid radicals. Thus, $2PbCO_3.Pb(OH)_2$ (white lead), $CuCO_3$, $Cu(OH)_2$ (melachite), $Pb(OH)NO_3$ (basic lead nitrate), $BiONO_3$ (basic bismuth nitrate) are the examples of basic salt.

(*b*) *Dialysis.*—Dialysis is the process by which a crystalloid is separated from a colloid by means of a semi-permeable membrane which is capable of allowing the crystalloid molecules to pass through it, but not the colloid particles.

Graham found that certain substances like gum, albumen, silicic acid, etc, in solution cannot pass practically through parchment, animal bladder, etc. whereas certain other substances like hydrochloric acid, common salt, nitre, etc. in solution readily pass through the parchment, animal bladder, etc.

Thus, a shallow bell jar open at both ends, but fitted with a piece of parchment paper or bladder at one end is kept partly immersed in water in another jar. Into the bell jar aqueous solution of potassium iodide is taken along with certain amount of starch also in solution. A little of this mixed solution when treated with chlorine water is turned blue. After a time it is found that potassium iodide has passed into the outer jar but not particles of starch present in the solution. It is proved by adding chlorine water to water present in the outer jar which turns brown due to liberation of iodine from KI.

The apparatus shown in the adjoining figure and used in the experiment is called a dialyser, and this process of separa-

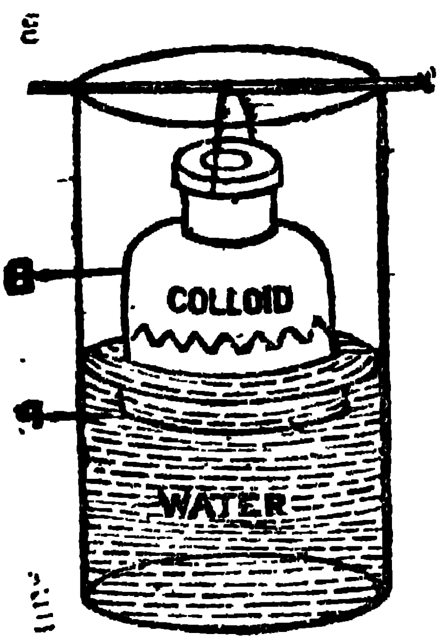


Fig. 67

tion of a colloid like starch from a crystalloid like potassium iodide is called dialysis.

(*c*) Dissociation is a temporary splitting up of molecules of a substance into simpler molecules or atoms which reunite under reversed experimental condition, the shifting taking place in such a fashion that a dynamic equilibrium is set up under all changed conditions between undecomposed molecules and the simpler compounds (or atoms of the same elementary substance) formed from it.

Thus, on heating, ammonium chloride dissociates into ammonia and hydrogen chloride and on cooling ammonium chloride is formed back, but during heating an equilibrium condition is set up depending on temperature, when rate of decomposition and of recombination of ammonia and hydrogen chloride is found to balance

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Similar is the case with iodine when on heating iodine molecule dissociates into iodine atoms.

$$I_2 \rightleftharpoons I + I.$$

(*d*) A catalytic agent is a substance which, when present in very small quantity, either increases or diminishes the velocity of a chemical reaction without itself undergoing any change in mass and in chemical composition, at the end of the reaction.

Thus, in preparing oxygen from potassium chlorate, manganese dioxide is added in small quantity to hasten the decomposition of potassium chlorate. MnO_2, is therefore, a catalytic agent in the reaction mentioned. Also phosphoric acid is added to hydrogen peroxide in small amount to retard the spontaneous decomposition of hydrogen peroxide. Thus phosphoric acid acts here as a catalytic agent.

(e) The mass, in grams, of an element which is liberated by the passage of unit quantity of electricity, that is, one coulomb, through the solution or fused compound of the element, is known as the *Electro-chemical Equivalent* of the element.

Thus, it is found that 1 coulomb of electricity liberates from the solution of an acid 0·0000104 gm. of hydrogen. Thus the electrochemical equivalent of hydrogen is 0·0000104. Similarly, when 1 coulomb of electricity, that is, 1 ampere of current flowing for 1 second, is passed through a solution of silver salt, 0·001118 gm. of silver is deposited on the cathode. Thus, 0·001118 is the electro-chemical equivalent of silver.

Q. 7. *How is the electrolysis of brine carried out on a large scale? What products are formed by this method?*

Describe briefly how you would prepare (a) solid sodium hydroxide, (b) hydrochloric acid and (c) a solution of sodium hypochlorite from these products.

Ans. The electrolysis of brine is carried out on a large scale in a rectangular vessel divided into three compartments by means of slate partitions (Fig. 68). The partitions do not actually touch the bottom of the vessel but dip into a layer of mercury which covers its floor. The two outer compartments are filled with *brine* and are fitted with stout carbon rods which serve as the **anodes. The cathode** is a bunch of iron rods suspended in the middle compartment containing water to which a little caustic soda has been added to make it a conductor. The layer of mercury is electrically connected with the iron rods. The whole vessel rests, on one side, upon an eccentric. The anodes are now connected together and then with the positive pole of a battery, while the cathode is connected with its negative pole. On passing electric current chlorine is evolved at the anode and is led away for the manufacture of bleaching powder. Sodium is liberated at the cathode in the outside compartments where it dissolves in mercury producing an amalgam. The amalgam is transferred to the middle compartment by giving a slow rocking movement to the whole vessel by the eccentric. Sodium reacts with water in the middle compartment producing caustic soda solution and hydrogen. The products obtained are chlorine, hydrogen and caustic soda solution.

(*a*) Solid sodium hydroxide is obtained from the caustic soda solution obtained by evaporating it in iron vessels. The solid residue so obtained is finally to be melted and cast into sticks, pellets or balls as the case may be.

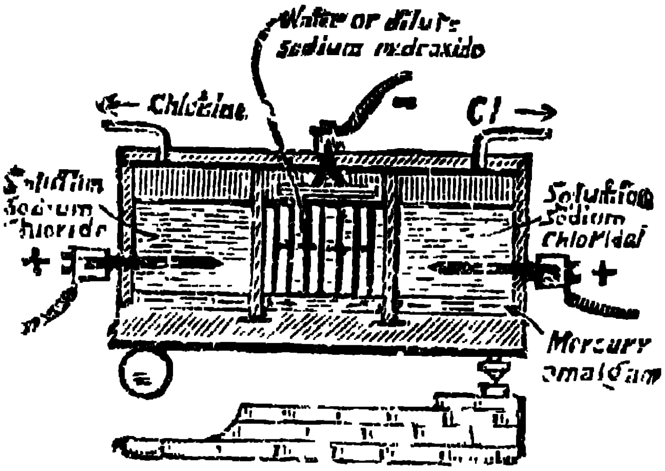


Fig. 68

(*b*) Chlorine obtained from the anode chambers and hydrogen obtained from the cathode chamber are mixed and burnt in a special burner when chemically pure hydrogen chloride is obtained. When it is dissolved in water. hydrochloric acid is produced.

$$H_2 + Cl_2 = 2HCl.$$

(*c*). Solution of caustic soda obtained in the middle compartment is taken out and somewhat diluted and then chlorine from the anode chambers is passed into it, leaving the solution alkaline. Sodium hypochlorite is formed along with sodium chloride and remains in solution.

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$

Q. 8. *How is cast iron prepared ? State its properties. How does it differ from* (*a*) *wrought iron and* (*b*) *steel ?*

Ans. The ores generally employed for the preparation of cast iron are the oxides and the carbonate. These ores are first roasted in order to drive off water and carbon dioxide, to render the mass porous and to convert the ferrous oxide to ferric oxide. The oxide, thus obtained, is then reduced with coke and limestone in a blast furnace. The blast furnace is made of steel and lined inside with fire-bricks. It is from 50 to 80 ft. in height and in modern American practice about 120 ft. in height, and is broadest at the middle. The top of the furnace

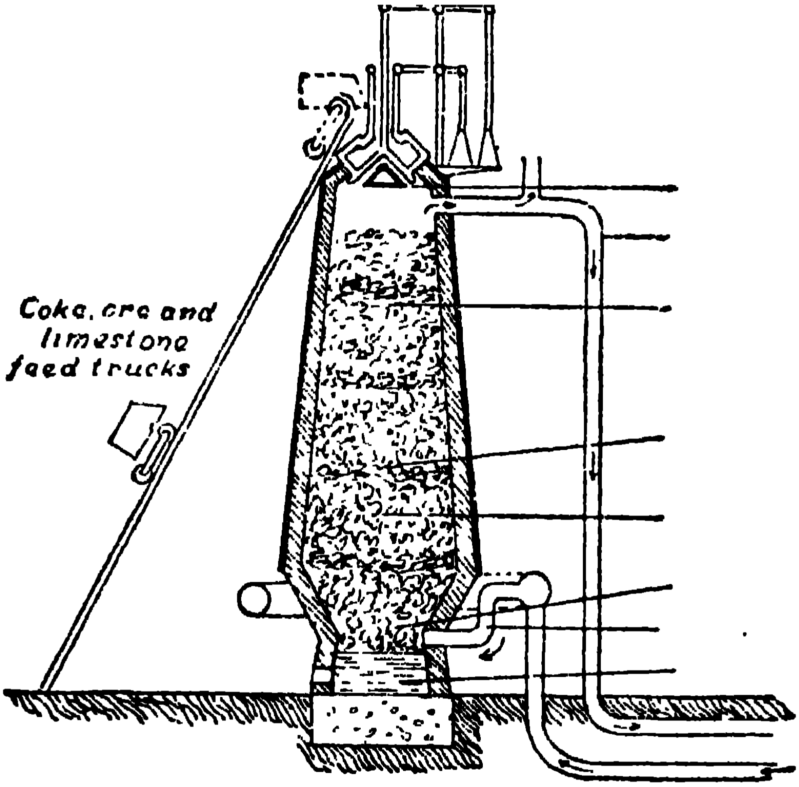


Fig. 69

is closed by a *cup-and-cone* arrangement. The calcined ore mixed with coke and limestone, is introduced into the furnace, by lowering the cone. A blast of heated air at a temp. of 700°—800°C. is then introduced through the jets at the bottom, known as tuyeres, placed round the base of the furnace. The oxygen of the air combines with the carbon to from carbon monoxide which brings about the reduction of the iron oxide to iron.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

A portion of Fe_2O_3 that may escape reduction by CO is reduced by carbon itself. The spongy iron, so produced at a temperature of 1000°C., absorbs various impurities like carbon, sulphur, phosphorus and silicon from the ore, coke, limestone etc. This impure iron melts and descends to the bottom of the furnace and collects there in the molten condition. Lime, obtained by the decomposition of the limestone added to the charge at the temperature of the furnace, combines with the siliceous impurities present in the ore forming a slag which flows down with the molten iron to the hearth. The slag, being lighter than the molten iron, floats on its surface, and thus prevents oxidation of the iron by the oxidising action of the blast.

$$CaCO_3 = CaO + CO_2$$
$$CaO + SiO_2 = CaSiO_3 \text{ (slag).}$$

As the slag reaches a certain height, it is taken out by opening certain holes, known as slag-notch, kept closed with clay ; the iron is run off at suitable intervals by opening certain other holes in the hearth also kept closed with clay. The molten iron is allowed to flow into moulds of sand. Iron, thus obtained, is known as *cast iron* or *pig iron.*

Properties of cast iron :—Cast iron contains 2 to 5 per cent. of carbon ; this carbon may be present in the free state or in combination with iron as Fe_3C. In the former case, the iron is called *grey cast iron* ; when treated with acids, it liberates hydrogen mixed with very little hydro-carbons and carbon separates out in the form of graphite. In the latter case, the cast iron is known as *white cast iron* ; when treated with acids, hydro-carbons are freely evolved along with hydrogen. Besides carbon, there are also present in cast iron silicon, phosphorus, sulphur and manganese in small proportions as impurities. Due to the presence of these impurities in such a high percentage, cast iron readily fuses (m. p. 1200°) and is brittle in character, so it cannot be worked under the hammer. It is crystalline in structure. It cannot be permanently magnetised.

(*a*) Cast iron differs from wrought iron in its carbon content and in containing other impurities. Cast iron .is the impurest form of commercial iron and it contains carbon to the extent of 2—5%, and other impurities like sulphur, phosphorus, silicon, manganese, etc. Wrought iron, on the other hand, is the purest form of commercial iron and it contains carbon to the extent of 0·12—0·25%, and other impurities are not present at all or are present only in traces. (b) Cast iron differs from steel with regard to carbon-content. Carbon is present to the extent of 0·25 to 1·5% in steel. Sulphur and phosphorus are reduced to negligible amount in steel. But inorder to improve the quality of steel, various elements like silicon, manganese, nickel, vanadium, tungsten etc. are introduced into steel. Thus steel is intermediate in composition to cast iron and wrought iron with regard to carbon content.

A general comparison of the three varieties of commercial iron, viz. cast iron, wrought iron and steel is given below :—

Properties	Cast iron	Wrought iron	Steel
1. Carbon content	2—5%	0·12 - 0·25%	0·25 - 1·5%
2. Impurities	Also impurities like Si, Mn, P, S. etc. are present	Purest form of commercial iron.	Intermediate in impurity between cast iron and wrought iron.
3. Hardness	Hard	Soft	Hard and soft
4. Malleability	Brittle	Malleable	Malleable and brittle.
5, Appearance	Crystalline	Fibrous	Crystalline.
6. Melting point	1200°C.	1500°C.	1300° - 1400°C.
7. Tempering	cannot be tempered	cannot be tempered	can be tempered.
8. Magnetisation	cannot be permanently magnetised.	cannot be permanently magnetised.	Can be permanently magnetised.

FIRST PAPER—1950

Q. 1. *State Faraday's laws of electrolysis. What is the relation (a) between the electro-chemical equivalent of an element and its chemical equivalent and (b) between the atomic weight of an element and its chemical equivalent ?*

Ans. Faraday's Laws of electrolysis are two in number, and these are :—

First Law :—The mass of an ion, liberated during electrolysis, is directly proportional to the quantity of electricity flowing through the electrolytic cell.

When 1 ampere of current flows through a circuit for 1 second, we get 1 coulomb of electricity or unit quantity of electricity flowing through the circuit. So the first law can be stated also as

"The mass of an ion, liberated during electrolysis, is directly proportional to the strength of the current as also to the time during which the current flows.

Mathematically stated, if W be the mass of an ion liberated by the passage of a current of C amperes flowing through the circuit for t seconds, then the law states,

$$W \propto ct,$$

or $W = zct$, where z is a constant called the Electrochemical equivalent of the ion. When $c = 1$ ampere, and $t = 1$ second, $z = W$, that is, Z is the amount of an ion liberated by the passage of 1 ampere of current for 1 sec.

Second Law :—When the same quantity of electricity is passed through several electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.

(*a*) From the second law of electrolysis, it follows that the Electrochemical equivalent (E. C. E.) of an element is directly proportional to its chemical equivalent.

Thus, if A and B be two elements,

$$\frac{\text{E.C.E. of } A}{\text{E.C.E. of } B} = \frac{\text{C. E. of } A}{\text{C. E. of } B}.$$

(*b*) We know that 12 parts by weight of Magnesium can displace 1 part by weight of hydrogen from hydrochloric acid. Therefore, by definition, 12 is the equivalent weight of magnesium.

But the atomic weight of magnesium is 24 when that of hydrogen is one.

Also 1 atom of magnesium can replace 2 atoms of hydrogen from two molecules of hydrochloric acid. Therefore the valency of magnesium is 2.

Hence the valency of magnesium $= 24 \div 12 =$ Atomic weight of magnesium $\div$ equivalent weight of magnesium.

This relationship can be shown in all other cases.

Therefore Atomic weight of an element = Its equivalent weight × its valency.

Q. 2. *Write notes on the following : (a) Super-saturated solution ; (b) Lixiviation ; (c) Mother liquor ; (d) Diffusion ; (e) Endothermic reaction ; (f) Acid salt.*

Ans. (*a*) A solution is said to be *super-saturated* with respect to a solute when somehow or other, a greater amount of solute remains dissolved in a given amount of solvent than what is required to get a saturated solution with that amount of solvent at a particular temperature. The solute will crystallise out immediately when a small fragment of it is added to the solution.

Thus, when some crystals of sodium thiosulphate, $Na_2S_2O_3, 5H_2O$, are heated in a closed flask, these melt in their own water of crystallisation. On cooling to the room-temperature, the crystals of sodium thiosulphate are not formed but what we get is super-saturated solution of sodium thiosulphate at room-temperature. On adding a tiny crystal of sodium thiosulphate to this super-saturated solution, it is found that the whole thing crystallizes out with much evolution of heat.

(*b*) *Lixiviation* is the process of bringing into solution only the soluble components of a mixture of substances by treating the mixture with a suitable solvent which can dissolve out the soluble components, thus effecting the separation of the soluble constituents from the insoluble residue.

Thus, black ash, obtained in the Leblanc process for manufacturing sodium carbonate, is crushed and treated with water, *i.e.*, lixiviated with water to dissolve out sodium carbonate which is soluble in water leaving the insoluble residue of the calcium sulphide and other impurities behind.

(*c*) When the solution of a solid in a liquid, saturated at a higher temperature, is allowed to cool down, a quantity of the solid held in solution, is deposited spontaneously in the crystal form. When these crystals are separated from the solution by filtration or otherwise, the liquid portion free from crystals is called *mother liquor*.

Thus, carnallite, $KCl,MgCl_2,6H_2O$ is first dissolved in water and the solution concentrated when potassium chloride crystallises out and is removed. The liquid portion that remains after the removal of potassium chloride crystals is called *mother liquor*, in this case special name of *bittern* being applied to it.

(*d*) *Diffusion* is a general term, applicable both to diffusion of gases and to diffusion of a solute in a dilute solution or pure solvent.

The natural process by which one gas disseminates through another gas is known as gaseous diffusion. Thus, if a jar of chlorine be placed beneath a jar of hydrogen, mouth to mouth, and the lids of the two gas jars removed, then chlorine diffuses against gravity into the upper jar and hydrogen diffuses into the lower jar though it is much lighter than chlorine. This intermingling can be proved by suitable tests.

Similarly, if a strong solution of copper sulphate be taken in a jar and cautiously covered with water without distributing the solution below, it will be found after a few days that copper sulphate has travelled upwards into the pure solvent making the solution homogonous. This is the diffusion of a solute into a solvent.

Now, gaseous diffusion can take place even when the gases are separated by a porous septum, the lighter gas diffusing more rapidly than the heavier one.

(*e*) When a chemical reaction takes place with the absorption of heat, it is said to be an endothermic reaction.

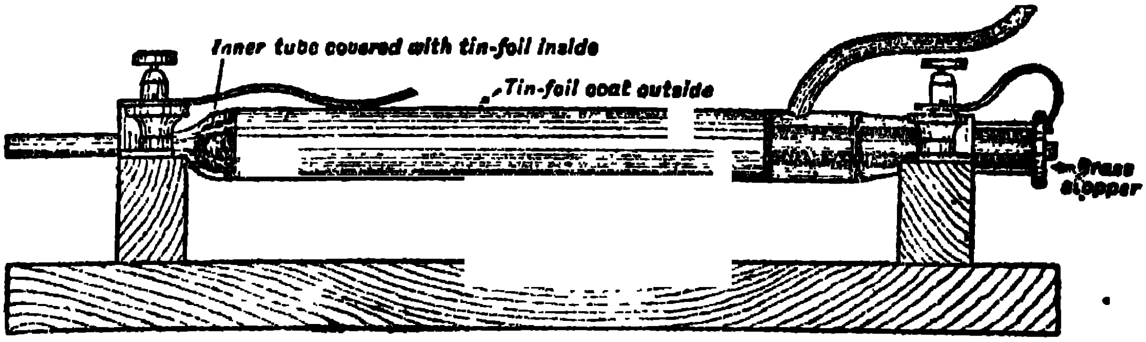
Thus, when *C* and *S* are made to combine by heating, much heat is absorbed in the formation of the compound carbon disulphide. Another example is the formation of nitric oxide, NO, from its elements nitrogen and oxygen, the reaction taking place only at the temperature of the electric arc.

(*f*) *Acid salt* : When the replaceable hydrogen atoms present in the molecule of a polybasic acid are *partially* replaced by a metal or a group of elements behaving like a metal (a radical), then the resultant salt is called an *Acid salt.* Thus, in sulphuric acid, H_2SO_4, there are two replaceable hydrogen atoms and when only one atom of hydrogen is replaced by a metal we get acid salt. Thus $NaHSO_4$, sodium hydrogen sulphate, is an acid salt.

Q. 3. *How is ozone prepared? Describe experiments to illustrate its properties. How was its molecular weight determined?*

Compare and contrast ozone and hydrogen peroxide.

Ans. Ozone is prepared by exposing pure, dry oxygen to the action of silent electric discharge in Siemen's ozoniser. The apparatus consists of two co-axial glass tubes, one fitted inside the other and hermetically sealed at one end. The outer tube has an inlet pipe near the sealed end and the other end is drawn out in order to form an exit tube. The outside of the outer tube and the inside of the inner tube are coated with tin-foils. These tin-foils are connected to the two binding screws fitted at the base of the apparatus, the two binding screws being in their turn in connection with the terminals of a Ruhmkorff's coil. Dry oxygen is passed through the annular space between the tubes in slow stream and a series of silent electric discharge passed through, so that the oxygen is subjected to an electrical



Siemens' ozoniser.

Fig. 70

strain. The gas that comes out of the exit contains a mixture of oxygen and ozone,

$$3O_2 = 2O_3.$$

The yield of ozone is only 5 to 8% of the oxygen used.

Experiments to illustrate the properties of ozone :—

Expt. 1. The gas ozone possesses a fishy odour as is ascertained by smelling it.

Expt. 2. Collect dry oxygen in a eudiometer tube fitted with Pt-wires at the top over conc. H_2SO_4. Pass sparkless discharge of electricity, with the help of Pt-wires from an induction coil through the dry oxygen. It is partially converted into ozone and there is contraction in volume. This shows that ozone is a condensed form of oxygen. Then introduce a little oil of turpentine into the eudiometer tube, there is further diminution in volume and it can be shown that ozone has disappeared.

This proves that ozone is absorbed by oil of turpentine.

Ozone is a strong oxidising agent.

Expt. 3. Dissolve sulphur dioxide gas in water and add $BaCl_2$ solution to it. A white ppt. is obtained. Add dil. HCl. to the precipitate, it dissolves.

Then take another portion of a solution of sulphur dioxide in water and pass ozone through it. Then add $BaCl_2$ solution. A white ppt. is obtained, but on addition of dil. HCl, the precipitate does not dissolve.

The reactions are explained as follows :—

$$SO_2 + H_2O = H_2SO_3$$
$$BaCl_2 + H_2SO_3 = BaSO_3 + 2HCl$$
$$BaSO_3 + 2HCl = BaCl_2 + SO_2 + H_2O.$$

So the precipitate dissolves in the first case.

$$3SO_2 + O_3 = 3SO_3$$
$$H_2O + SO_3 = H_2SO_4$$
$$BaCl_2 + H_2SO_4 = BaSO_2 + 2HCl.$$

$BaSO_4$ is insoluble in dil. HCl.

Expt. 4. Take a piece of filter paper, soak it with lead acetate solution. Expose this moist lead acetate paper to H_2S gas coming out from Kipp's apparatus. It turns black due to the production of lead sulphide. This paper containing moist black lead sulphide is exposed to ozonised oxygen. The black colour disappears.

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

Expt. 5. Take a piece of starch-iodide paper, moisten it with water and expose it to the action of ozonised oxygen. The paper turns blue due to liberation of iodine from potassium iodide by oxidation and this iodine produces blue coloration with starch present.

$$2KI + O_3 + H_2O = O_2 + I_2 + 2KOH.$$

The molecular weight of ozone was determined by Soret by performing diffusion experiment and applying Graham's law of diffusion, the density of ozone was found out and density × 2 was the molecular weight. The difficulty encountered in this experiment was that ozone was not obtained pure, but admixed with oxygen. In order to get over this difficulty of the dilution of ozone with oxygen, Soret allowed the gases, ozonised oxygen and chlorine (or carbon dioxide) to diffuse into pure oxygen, and measured the relative rate of diffusion v/V of each gas mixed with oxygen, where v is the volume of gas diffusing and V the total volume present in the original mixture. The rate of diffusion of oxygen in both directions was the same in all cases. The ratios $\frac{v}{V}$ were therefore proportional inversely to the square roots of the densities of the diffusing gases.

Recently, by a determination of the vapour density of *pure* ozone by Dumas' method, the molecular weight of ozone has been arrived at by Riesenfield.

Comparison and contrast between Hydrogen peroxide and ozone.

Ozone	*Hydrogen peroxide*
1. Ozone is a gas.	1. Hydrogen peroxide is a syrupy liquid.
2. It has a fishy odour.	2. It is odourless.

Ozone	*Hydrogen peroxide*
3. It liberates iodine from neutral or acidified solution of potassium iodide, but in presence of ferrous sulphate, ozone cannot liberate iodine from potassium iodide solution.	3. It can liberate iodine from potassium iodide solution even in presence of ferrous sulphate.
4. Ozone turns paper soaked in an alcoholic solution of tetramethyl base purple-violet.	4. Hydrogen peroxide has no action on tetramethyl base paper.
5. Ozone does not produce any coloration with $K_2Cr_2O_7$ solution acidified with H_2SO_4.	5. Hydrogen peroxide produces an azure-blue coloration with $K_2Cr_2O_7$ solution acidified with H_2SO_4. The blue colour can be extracted with ether when shaken with it.
6. Ozone does not produce any coloration with titanium salt solution.	6. Hydrogen peroxide turns titanium salt solution orange-yellow.
7. Ozone cannot decolorise acidified $KMnO_4$ solution.	7. Hydrogen peroxide at once decolorises an acidified solution of $KMnO_4$. $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$.

Q. 4. *What are the common sources of bromine? How is bromine manufactured industrially? State its properties and uses. Name an important bromide and state its use.*

Ans. The common sources of bromine are : (1) bittern, or the mother liquor obtained after the crystallisation of potassium chloride and its removal from a solution of Stassfurt carnallite, KCl, $MgCl_2$, $6H_2O$ which contains $MgBr_2$ as impurity; (2) Sea-water, average sea-water contains 0·015 per cent, of bromine.

Bromine is at present manufactured industrially in American practice from sea-water off the North Carollina coast. The sea-water is acidified and then treated with chlorine. The bromine liberated is blown out by a current of air and absorbed in a solution of sodium carbonate, when a mixture of sodium bromide and sodium bromate is formed. The solution is next rendered acidic, when bromine is liberated and distilled off in steam.

$$3Br_2 + 3Na_2CO_3 = 5NaBr + NaBrO_3 + 3CO_2$$
$$NaBrO_3 + 5NaBr + 6HCl = 3Br_2 + 6NaCl + 3H_2O.$$

Properties of bromine.—Bromine is a dark-red liquid at ordinary temperature. It is a heavy liquid, the density being 3·119 at 20°C. It gives off spontaneously a dark-red poisonous vapour, of most irritating odour. The vapour attacks the mucous membranes of nose and throat very vehemently. It attacks also skin producing corrosive sores which are very difficult to heal up. Its boiling point is 59°. The vapour density at 228° corresponds to the molecular formula Br_2. At 1040°, the vapour of bromine dissociates to the extent of 6·3 per cent. $Br_2 \rightleftharpoons Br + Br$. Bromine dissolves in water and the solution is called *bromine water.* It also dissolves in alcohol, ether, chloroform, carbon disulphide and acetic acid. When bromine is passed into ice-cold water, bromine hydrate, $Br_2.8H_2O$ is obtained as a red solid. Bromine is neither combustible, nor ordinarily a supporter of combustion.

A jet of burning hydrogen when introduced into bromine vapour continues to burn forming HBr, but at ordinary temperature H_2 and Br_2 do not combine. Bromine combines directly with many elements, forming bromides. It is a mild oxidising agent and oxidises sulphites to sulphates.

$$Na_2SO_3 + Br_2 + H_2O = Na_2SO_4 + 2HBr.$$

Bromine vapour possesses mild bleaching properties, it bleaches moist litmus paper, but more slowly than chlorine.. Bromine-water decomposes on exposure to light giving off oxygen. $2H_2O + 2Br_2 = 4HBr + O_2$. With cold caustic soda or potash solution, bromine produces hypobromite and bromide, whereas with hot solution of alkalies, bromate and bromide are obtained.

$$Br_2 + 2KOH = KBr + KOBr + H_2O$$
$$3Br_2 + 6KOH = KBrO_3 + 5KBr + 3H_2O.$$

Uses of bromine.—Bromine is used to a certain extent as a disinfectant. For this purpose, bromine is absorbed in Kieselguhr and cut in the form of cubes and sold under the trade name *bromum solidificatum.* It is also employed as a mild oxidising agent and in synthetic organic chemistry, *e.g.*, in the preparation of the dye eosin and of the antiknock agent lead tetraethyl through ethylene dibromide used along with motor fuels. Bromine is also employed in the preparation of certain important bromides.

·One important bromide to be mentioned is potassium bromide. It is used in medicine as also in the production of silver bromide which in its turn is employed in photography.

Q. 5. *How are the following prepared* :—(*a*) *Green vitriol* ; (*b*) *white lead* ; (*c*) *Arsenious oxide* ; (*d*) *Stannous chloride* ; (*e*) *Carbon bisulphide ?*

State their uses.

Ans. (*a*) Iron wire or ferrous sulphide is dissolved in dilute sulphuric acid, the solution filtered and the filtrate concentrated to crystallisation when green crystals of $FeSO_4$, $7H_2O$ are obtained. This material is manufactured by exposing heaps of marcasite (FeS_2) to air in the presence of moisture. The resulting sulphuric acid is treated with scrap iron and the mass is lixiviated with water. The solution is allowed to settle in lead-lined vats and the clear supernatant liquid is drawn off and allowed to crystallize after concentrating it by passing steam through the pipes placed inside the solution.

$$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4.$$

Green vitriol can be obtained as a by-product in the preparation of H_2S in a Kipp's apparatus in the laboratory. The solution left behind in the H_2S—Kipp, when filtered and concentrated, yields crystals of $FeSO_4$, $7H_2O$.

Uses :—Green vitriol is used in dyeing, in the preparation of jeweller's rouge, and in the manufacture of writing ink.

(*b*) *White lead*—It is manufactured by the Dutch Process which gives the best product. Lead grids or perforated discs of lead are placed above a little vinegar in small earthenware pots. These pots are placed on the floor of a shed which is covered with spent tan-bark or horsedung. The pots are covered with wooden planks, on which are placed more of tan-bark or horsedung and then similar pots. Successive layers of wooden planks and pots are placed one above the other until the shed is full. The whole is now allowed to stand for 6 to 10 weeks. During the time tan-bark or horsedung undergoes fermentation, which generates heat and carbon dioxide. Heat vaporises acetic acid which in presence of atmospheric oxygen and moisture attacks lead forming basic lead acetate. This basic acetate of lead is afterwards converted by CO_2 and heat generated by fermentation into basic lead carbonate, $2PbCO_3, Pb(OH)_2$, regenerating acetic acid. The pots are then taken out, the product is removed by hammering which flattens out any unchanged lead and then it is ground to powder, washed with water, dried and sent out to the market.

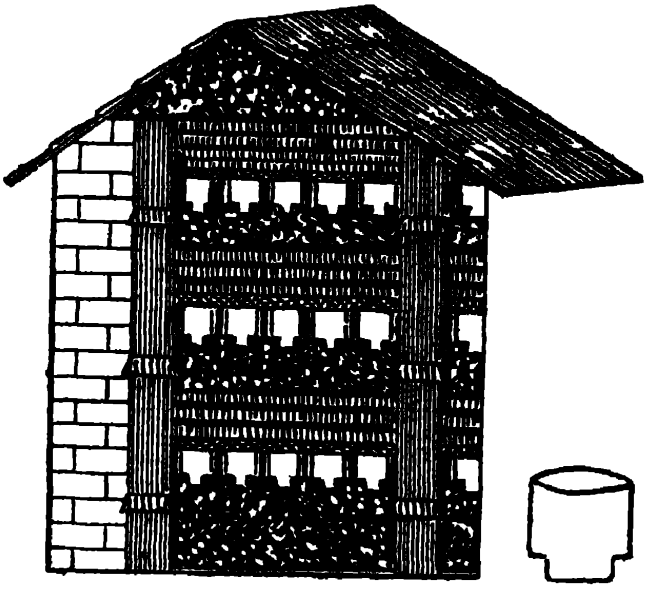


Fig. 71

$$2Pb + 2H_2O + O_2 = 2Pb(OH)_2$$
$$Pb(OH)_2 + 2CH_3COOH = Pb(CH_3COO)_2 + 2H_2O$$
$$Pb(CH_3COO)_2 + Pb(OH)_2 = Pb(CH_3COO)_2, Pb(OH)_2$$
$$3\{Pb(CH_3COO)_2, Pb(OH)_2\} + 4CO_2 + 2H_2O$$
$$= 2[2PbCO_3, Pb(OH)_2] + 6CH_3COOH.$$

Uses.—White lead is chiefly used as a pigment, and sometimes in the manufacture of flint glass.

(*c*) Arsenious oxide is obtained by roasting minerals containing arsenic in the revolving calcinor of Oxland and Hocking, a rotating iron cylinder lined with refractory material, down which the crushed ore slides from a hopper above. Usually mispickel, FeAsS, is used. The ore meets the flames and hot gases from a furnace at the lower end. The arsenical soot is collected in flues. This impure arsenious oxide is purified by sublimation in iron pots.

$$2FeAsS + 5O_2 = Fe_2O_3 + As_2O_3 + 2SO_2.$$

Arsenious oxide is used in small doses in medicine and it is used for the preparation of other arsenic compounds. (*This is beyond the Intermediate Syllabus.*)

(*d*) *Stannous chloride.*—The anhydrous salt is prepared by passing dry HCl gas over heated metallic tin. The hydrated salt is prepared by boiling granulated tin or tin-foil with conc. HCl, preferably in presence of a few bits of Pt-foil.

$$Sn + 2HCl = SnCl_2 + H_2.$$

The solution is filtered and evaporated to crystallization when crystals of $SnCl_2, 2H_2O$ separate out. This is known technically as *tin salt.*

Uses.—It is used as a mordant in dyeing industry and as a reducing agent in the laboratory.

(*e*) Carbon disulphide is prepared by passing sulphur vapour over red-hot carbon. The reaction is endothermic.

$$C + 2S = CS_2.$$

The reaction is carried out in Taylor's electric furnace. A tower 40 ft. in height and 16 ft. in diameter is used. It is packed with charcoal or coke from the top. There are four carbon electrodes set below this charcoal layer in a furnace, between alternate pairs of which an electric arc is struck. Sulphur placed in the lower part of the furnace melts and evaporates, the vapour passing through red-hot charcoal bed above the arc. CS_2 is formed and leaves the furnace at the top in the form of vapour which can be condensed by cooling to liquid state.

Carbon disulphide is used to kill moths in furs, etc. and mice and rats in grain elevators and also as a solvent in the laboratory.

Q. 6. *How is metallic sodium obtained from caustic soda? State the properties and uses of the metal.*

Ans. Metallic sodium is obtained from caustic soda by the electrolysis of fused caustic soda in a Castner cell and so the process is known as Castner's process.

Caustic soda is contained in an iron pot, set in suitable brick work, and is kept in a melted condition by gas flames below.

Through the bottom of this vessel passes an iron rod kept in the vertical position by the caustic soda in the lower and narrow part of the vessel, caustic soda there being in the solidified state. The anode is a cylinder of nickel, suspended from and kept surrounding the cathode, and is prevented from touching the iron cathode by means of a nickel wire-gauze cylinder which hangs from a cylindrical iron vessel which is open at the bottom and provided with a lid at the top and is kept hanging from the top of the iron vessel just above the iron cathode. Electric

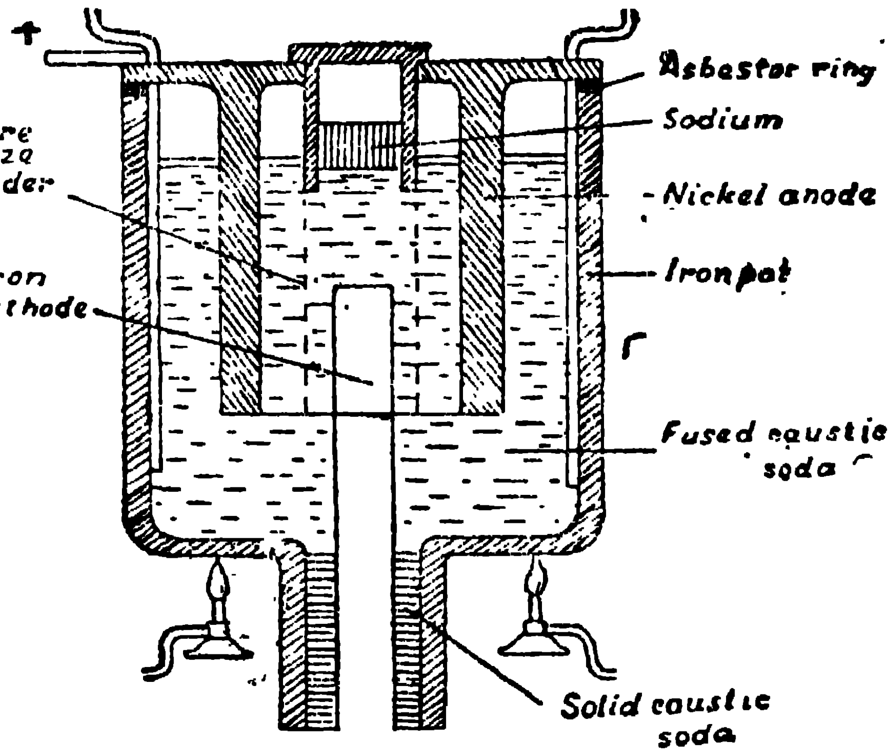


Fig. 72

current is passed by connecting the electrodes to the poles of a battery. The fused caustic soda is decomposed. Sodium is liberated at the cathode, and being lighter than fused NaOH, rises up to the surface and collects inside the iron vessel hanging over the cathode, in which hydrogen also collects. This hydrogen protects sodium from oxidation. The excess of hydrogen escapes through the lid. Oxygen is liberated at the anode and escapes through an out-let at the top, Sodium is removed by means of perforated ladles from time to time and is kept under Kerosine oil

$$2NaOH = \underbrace{2Na + H_2}_{\text{Cathode}} + \underset{\text{Anode}}{O_2}$$

Properties of sodium.—Sodium is a soft, silver-white metal. It is so soft that it can be cut with a pen-knife. Its sp. gr. is 0·97 and being lighter than water, it floats on water. Perfectly dry air or oxygen is without action on sodium. But moist air tarnishes it on the surface through the formation first of Na_2O which is ultimately changed to Na_2CO_3 due to the action of moisture and atmospheric CO_2. On this account metallic sodium is kept under kerosine oil. When ignited in oxygen it burns with a golden yellow flame producing sodium monoxide and sodium peroxide, Na_2O_2. Sodium reacts with water at ordinary temperature to give caustic soda and hydrogen.

$$2Na + 2H_2O = 2NaOH + H_2.$$

When heated in dry hydrogen gas at 365° sodium hydride is formed.

$$2Na + H_2 = 2NaH.$$

With mercury it forms an amalgam.

$$Na + Hg = NaHg.$$

The amalgam also decomposes water, evolving hydrogen.

Uses of Sodium.—Sodium is used for the manufacture of sodium peroxide and sodium cyanide ; for the extraction of metallic magnesium, aluminium, elementary boron and silicon. Sodium amalgam is used as a reducing agent. An alloy of sodium and potassium is used in high temperature thermometry.

Q. 7. *20 c.c. of a pure hydrocarbon is mixed with 80 c.c. of oxygen and exploded. The volume after explosion is 60 c.c.*

After shaking with caustic potash solution the volume is 20 c.c. What is the hydrocarbon ?

Ans. It can be shown that immediate contraction on explosion = volume of hydrocarbon taken + volume of oxygen used up − volume of carbon dioxide produced.

Here, immediate contraction after explosion = (20 + 80 − 60) c.c. = 40 c.c. and volume of carbon dioxide produced = (60 − 20) c.c. = 40 c.c.

Hence 40 = 20 + vol. of O_2 used up − 40 ∴ vol. of O_2 used up = 60 c.c. Now, carbon dioxide contains its own volume of oxygen. Therefore, in the formation of 40 c.c. of CO_2, 40 c.c. of O_2 were used up. Hence, the remaining 20 c.c. of O_2 had been used up in forming water by combining with hydrogen of the hydrocarbon. Now, 20 c.c. of O_2 can combine with 40 c.c. of hydrogen to form water and these 40 c.c. of hydrogen must have come from 20 c.c. of the hydrocarbon taken. Thus, the hydrocarbon contains twice its volume of hydrogen. Hence, 1 vol. of hydrocarbon contains 2 vols. of hydrogen.

Then, by Avogadro's hypothesis, if *n* be the number of molecules present in 1 vol. of hydrogen,

n mols. of hydrocarbon contain 2*n* mols. of hydrogen,

or, 1 mol. of hydrocarbon contains 2 mols. or 4 atoms of hydrogen, since hydrogen molecules are diatomic.

Thus, the formula of the hydrocarbon is C_xH_4.

To determine x :—

20 c.c. of the hydrocarbon give on explosion 40 c.c. of carbon dioxide or 1 vol. of the hydrocarbon gives rise to 2 vols. of carbon dioxide, *i.e.*, *n* mols. of the hydrocarbon produce 2*n* mols. of carbon dioxide or, 1 mol. of the hydrocarbon gives 2 mols. of carbon dioxide. But each molecule of carbon dioxide contains one atom of carbon. Hence, 2 mols. of carbon dioxide contain 2 atoms of carbon and these two atoms of carbon must have come from 1 mol. of the hydrocarbon. Thus $x = 2$ and the formula for hydrocarbon is C_2H_4. The hydrocarbon is ethylene.

Q. 8. *How is phosphine prepared in the laboratory? Give a neat sketch of the apparatus and give equation of the reaction that occurs.*

Compare the properties of phosphine with those of ammonia and arsine.

Ans. Phosphine, PH_3, is prepared in the laboratory by heating white phosphorus with a concentrated solution of caustic soda in a flask provided with an inlet tube reaching nearly to its bottom and a delivery tube, both being fitted through the cork closing the flask in an air-tight fashion. The inlet tube is connected with a laboratory gas-tap or a hydrogen-generating Kipp's apparatus. The delivery tube is dipped under water in a pneumatic trough.

A small quantity of white phosphorus and a 30 per cent. solution of caustic potash or caustic soda are taken in the flask. The air in the flask is then chased out by coal gas or by hydrogen from the Kipp, as the case may be; otherwise explosion will take place. When all the air has been driven out, the flask is heated after being placed over a wire gauze. Phosphine is evolved as gas, and as each bubble of gas escapes through water in the pneumatic trough, it catches fire and burns producing vortex rings of white smoke (metaphosphoric acid) as shown in the figure.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3$$

sodium hypophosphite.

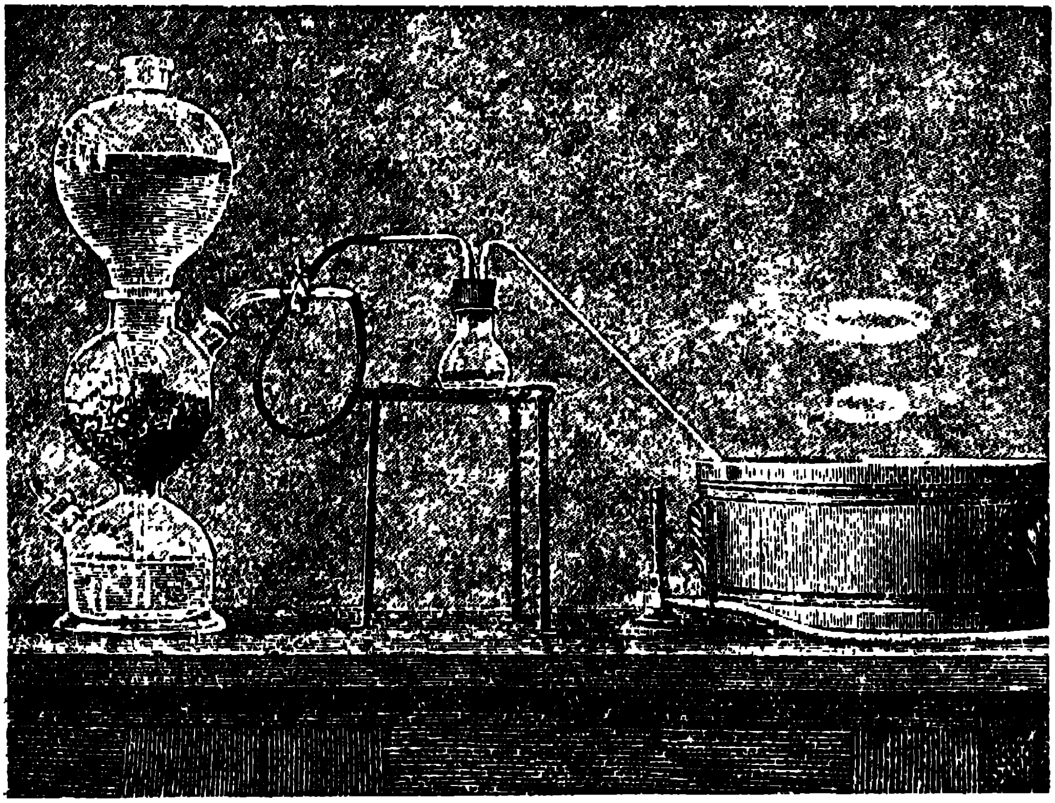


Fig. 73

Comparison of Phosphine with Ammonia.

Phosphine, PH_3	Ammonia, NH_3
(1) It is a colourless gas, with the smell of rotten fish.	(1) It is a colourless gas, with a very pungent odour.
(2) It is heavier than air.	(2) It is lighter than air.
(3) It is poisonous.	(3) It is of non-poisonous nature.
(4) It is very slightly soluble in water ; the solution is non-alkaline and does not turn red litmus solution blue.	(4) It is extremely soluble in water ; the solution is alkaline and turns red litmus solution blue.
(5) Phosphine is feebly basic, and produces phosphonium compounds only with halogen acids, specially under pressure. $PH_3 + HI = PH_4I$ etc.	(5) Ammonia is distinctly basic and gives ammonium compounds with acids. $NH_3 + HI = NH_4I.$ $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$
(6) It may be obtained by heating PH_4I with alkalies.	(6) It is obtained by heating ammonium salts with alkalies.
(7) Phosphine spontaneously burns in chlorine $PH_3 + 4Cl_2 = PCl_5 + 3HCl$ $PH_3 + 3Cl_2 = PCl_3 + 3HCl$	(7) Ammonia reacts with chlorine with evolution of heat and light giving N_2 and sometimes NCl_3, when Cl_2 is in excess. $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$ $NH_3 + 3Cl_2 = NCl_3 + 3HCl.$
(8) When phosphine is passed into metallic salt solutions in water, phosphides of the metals are precipitated. $3CuSO_4 + 2PH_3 = 3H_2SO_4 + Cu_3P_2$	(8) When ammonia is passed into aqueous solutions of metallic salts, hydroxides of the metals are usually precipitated. $CuSO_4 + 2NH_3 + 2H_2O = Cu(OH)_2 + (NH_4)_2SO_4$ **N. B.** In excess of ammonia $Cu(OH)_2$ dissolves. $Cu(OH)_2 + 4NH_4OH$ $[Cu(NH_3)_4](OH)_2 + 4H_2O.$

SECOND PAPER

Q. 1. *Explain what is meant by a 'normal solution'. How does it differ from a 'molar' solution of a substance ?*

What weight of sodium carbonate, sodium bicarbonate and sulphuric acid will be required to prepare a normal solution of each.

Calculate the quantity of a sample of sodium carbonate, which contains 90 per cent. carbonate and 10 per cent. bicarbonate, that should be dissolved in water to make one litre solution, so that it will require an equal volume of $\frac{N}{5}$ *sulphuric acid solution for complete neutralization.*

(Na = 23·O, C = 12·O, S = 32·O)

Ans. A normal solution of any substance is that which contains a gram equivalent of that substance dissolved in a litre of its solution.

A 'molar' solution of a substance is one which contains one gram-molecule of the substance dissolved in a litre of its solution. Now, for substances like monobasic acids, monacid bases and salts of the type NaCl, in which one equivalent of the active element is present in the molecular weight of the substance, the gram-equivalent of the substance is the same as its gram-molecule. In their cases, the normal solution is identical with the molar solution. Thus, with HCl, 36·5 grams of the acid will be present in a litre of both the normal and gram-molecular solution. Such is also the case with NaOH or NaCl. But in the case of H_2SO_4, gram-equivalent of the acid is 49 grams, whereas the gram-molecule is 98 grams. Therefore, the normal solution of sulphuric acid will contain 49 grams of sulphuric acid in a litre of its solution, whereas, the molar solution of sulphuric acid will contain 98 grams of the acid in a litre of its solution. Also, in case of salt like Na_2CO_3, gram-equivalent is half its molecular weight, *viz.*, 53 *g.* whereas gram molecule means 106 grams. Hence a normal solution of Na_2CO_3 will contain 53 grams in a litre of its solution, whereas a molar solution will contain 106 grams per litre of its solution.

The gram-molecule of Na_2CO_3 is 106 grams, and so its equivalent weight in grams is 53, since it contains two atoms of the active element, sodium. Hence 53 grams of sodium carbonate are to be used in preparing a litre of its solution, for getting a normal solution of Na_2CO_3.

In the case of sodium bicarbonate, $NaHCO_3$, the gram-molecule is 84 grams and since it contains one equivalent of the active element sodium, its molecular weight is the same as its equivalent weight. So, for preparing a normal solution of $NaHCO_3$, 84 grams of this substance is to be used to prepare a litre of its solution.

The gram-molecule of sulphuric acid, H_2SO_4, is 98 grams, but its gram-equivalent is 49 grams, since it contains 2 atoms of the active element, hydrogen. Hence, 49 grams of sulphuric acid is to be dissolved in a litre of its solution to get a normal solution of this substance.

Sum.—Since one litre of the carbonate solution is neutralised by an equal volume of $\frac{N}{5}$ sulphuric acid, the carbonate solution is $\frac{N}{5}$ with regard to the mixture of carbonate and bicarbonate. Since normal solution of sodium carbonate contains 53 grams of Na_2CO_3 per litre of solution, $\frac{N}{5}$ solution will contain $\frac{53}{5}$ or 10·6 grams of Na_2CO_3.

Let x grams of the sample of sodium carbonate supplied be required to prepare this $\frac{N}{5}$ solution.

It contains $0·9x$ grams of Na_2CO_3 and $0·1x$ grams of $NaHCO_3$. Then, since 53 grams. of $Na_2CO_3 \equiv 84$ grams of $NaHCO_3$, therefore $0·1x$ grams of $NaHCO_3 \equiv 0·1x \times \frac{53}{84}$ grams of Na_2CO_3. Then by the question,

$$0·9x + \frac{5·3x}{84} = 10·6$$

$$\text{or,}\quad 0·9x + ·063x = 10·6$$

$$\text{or,}\quad 0·963x = 10·6$$

$$\therefore \quad x=\frac{10{\cdot}6}{0{\cdot}963}=11{\cdot}0 \text{ nearly.}$$

Therefore 11 grams of the sample of sodium carbonate containing sodium bicarbonate will be required to prepare the solution mentioned.

Q. 2. *Describe how you would determine the volumetric composition of sulphur dioxide and deduce its molecular formula therefrom.*

Calculate the volume of air at 30°C. and 750 mm. pressure that will be required for the complete combustion of 5 grams of a sample of pyrites containing 40 per cent. of sulphur, assuming that air contains 20 per cent. of oxygen by volume.

Ans. Volumetric composition of sulphur dioxide is determined by taking U-shaped eudiometer tube, open at one end and provided with a bulb at the other, as shown in Fig. 17 p. 82. The bulb is fitted with an air-tight glass stopper having two stout copper wires, one of which carries a copper spoon fitted to it. The spoon and the other wire are connected by a platinum spiral. There is a stop-cock fitted at the bottom of the open limb as shown in the figure. A small fragment of *pure* sulphur is taken on the spoon and the U-tube is filled completely with mercury. Pure dry oxygen is introduced in the U-tube by displacement of mercury in the limb fitted with the bulb. The stopper carrying the spoon containing pure sulphur is then replaced. The mercury level is then adjusted to the same height in both the limbs. The volume of oxygen is then noted. The copper wires are connected with the two terminals of a battery and electric current is passed through the Pt-wire. The Pt-wire becomes red-hot and ignites the piece of sulphur. Sulphur dioxide is produced and oxygen is used up. At first the mercury is depressed in the limb carrying the bulb owing to the thermal expansion of the volume of the gas. When the reaction is over, the apparatus is allowed to cool. Mercury is then found to stand exactly at the same level in both the limbs as before. Thus the volume of sulphur dioxide produced is exactly the same as the volume of oxygen used up.

Hence, sulphur dioxide contains its own volume of oxygen.

Thus, from the experiment, we know that 1 vol. of sulphur dioxide contains 1 vol. of oxygen. Let '*n*' be the number of molecules present in 1 vol. of sulphur dioxide. Then by Avogadro's hypothesis, *n* molecules of sulphur dioxide contain *n* molecules of oxygen, or 1 mol. of sulphur dioxide contains 1 mol. of oxygen, *i.e.*, 2 atoms of oxygen, since oxygen molecule is diatomic. (Deduction from Avogadro's hypothesis). Therefore, the formula of sulphur dioxide is S_xO_2, where x is an integer.

Now, the density of sulphur dioxide, as determined by experiment, is 32. Therefore, its molecular weight = 64. But 32 is contributed by 2 atoms of oxygen. Thus, 32 of the molecular weight of sulphur dioxide is contributed by sulphur. But 32 is the atomic weight of sulphur and thus it stands for 1 atom of sulphur.

Hence $x = 1$, and the molecular formula of sulphur dioxide is SO_2.

If the sample of pyrites be pure FeS_2, it would have contained 53·3% S and 46·7% Fe. But since the sample contains 40% S, there are impurities (like silica) present in the sample and so it contains proportionate iron, *viz.*, $\frac{46{\cdot}7 \times 40}{53{\cdot}3}$ or 35% nearly of iron.

So, 5 grams of the sample contain $\frac{5 \times 4\cancel{0}}{10\cancel{0}}$ or, 2 grams of sulphur and $\frac{\cancel{5} \times 35}{\underset{20}{1\cancel{0}\cancel{0}}}$ or, 1·75 grams of iron.

Now from the equations,

$$\underset{32}{S} + \underset{32}{O_2} = SO_2$$

$$\text{and } \underset{4\times 56}{4Fe} + \underset{3\times 32}{3O_2} = 2Fe_2O_3$$

we know that 32 grams of sulphur require 32 grams of oxygen, or 22·4 litres of oxygen at N.T.P., for complete combustion and 4 × 56 grams of iron require 3 × 32 grams of oxygen, or 3 × 22·4 litres of oxygen at N.T.P. for its complete combustion, the volumes being computed on the basis that the molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P.

Therefore, 2 grams of sulphur will require $\frac{2 \times 22{\cdot}4}{32}$ litres or 1·4 litres of oxygen at N.T.P. for complete combustion and 1·75 grams of iron will require $\frac{1{\cdot}75 \times 3 \times 22{\cdot}4}{56 \times 4}$ litres or 0·525 litres of oxygen at N.T.P. for complete combustion. Therefore total volume of oxygen required = 1·925 litres at N.T.P. Since air contains 20 per cent, of oxygen by volume, therefore volume of air required $= \frac{1{\cdot}925 \times 100}{20}$ litres at N.T.P. = 9·625 litres at N.T.P.

Let V be the volume of air at 30°C. and 750 mm. pressure. Then, by Boyle's and Charles' laws, we have

$$\frac{9{\cdot}625 \times 760}{273} = \frac{V \times 750}{273 + 30}$$

Therefore,

$$V = \frac{9{\cdot}625 \times 760 \times 303}{273 \times 750} \text{ litres}$$

$= 10{\cdot}82$ litres

= Volume of air required for complete combustion of 5 grams of the sample of pyrites, measured at 30°C. and 750 mm. pressure.

Q. 3. *Both air and nitrous oxide contain nitrogen and oxygen. How would you prove that in the one they are present as a mechanical mixture and in the other as a chemical compound ?*

You are given three cylinders containing nitrous oxide, nitric oxide and air respectively. Describe experiments by which you can distinguish between them.

How can nitric oxide be converted into nitric acid and the latter back again into nitric oxide ? Give equations.

Describe what happens when nitric oxide is passed into a solution of ferrous sulphate.

Ans. Air is a mechanical mixture of nitrogen and oxygen, whereas nitrous oxide is a chemical compound of nitrogen and oxygen.

The following are the reasons for considering air to be a mechanical mixture of nitrogen and oxygen :—

(1) In a mechanical mixture of two or more substances the properties of the different ingredients are retained, but when a compound is formed from two or more ingredients, the molecules of the ingredients are changed and new molecules are formed. These new molecules have properties altogether different from those of the molecules of the ingredients.

Thus, the properties of both nitrogen and oxygen are found to be present in air ; for example, oxygen is a supporter of combustion, so is also air, though to a less extent, on account of its dilution with nitrogen. Oxygen is absorbed by alkaline pyrogallate, while oxygen present in air is also absorbed by alkaline pyrogallate. But alkaline pyrogallate cannot remove oxygen by absorption from any of the oxides of nitrogen which are compounds of nitrogen and oxygen. After removal of oxygen from air by absorption with alkaline pyrogallate, nitrogen left shows all the properties of nitrogen.

Therefore air is considered to be a mechanical mixture.

(2) The analyses of samples of air drawn from different localities and different altitudes show that the proportion of nitrogen and oxygen in air by weight is *nearly* constant, yet slight variations are noticeable. But even the slightest deviation from constancy in composition is not possible in the case of a chemical compound.

Air is therefore considered to be a mixture of oxygen and nitrogen.

(3) When gases combine chemically, there is always a thermal effect, and oftentimes a change in volume is observed. But when 23 parts by weight of oxygen are mixed with 77 parts by weight of nitrogen, there is neither any heat change nor any change in volume yet the mixture behaves in every way like ordinary air.

Thus, air is a mechanical mixture.

(4) The density and other physical properties of air are average of those properties of the constituents, nitrogen and oxygen, in the proportion in which they are present in air. Thus, taking *d* to be the density of air which contains nitrogen and

oxygen in the proportion 4 : 1 by volume approximately, we can calculate d as follows :—

Weight of air = Weight of nitrogen + Weight of oxygen. Taking into consideration 100 vols. of air formed by the admixture of 80 vols. of nitrogen and 20 vols. of oxygen,

$$\begin{aligned} 100 \times d &= 80 \times 14 + 20 \times 16 \\ &= 1120 + 320 \\ &= 1440 \\ \therefore d &= 14{\cdot}4 \end{aligned}$$

The observed density of air is also 14·4 – just the value calculated on the assumption that air is a mechanical mixture.

Therefore air is nothing but a mechanical mixture.

(5) There are five different oxides of nitrogen whose gravimetric compositions are such that they obey the *Law of Multiple proportions*. The composition of air by weight (77 nitrogen : 23 oxygen) is such that no simple formula can be assigned to it. (77 parts by weight of nitrogen stand for 5½ atoms of nitrogen and 23 parts by weight of oxygen stand for 1·4375 atoms of oxygen.) Thus the Law of Multiple Proportions as applied to the case of definite oxides of nitrogen cannot be applied here.

Therefore air is a mechanical mixture. Also if a formula for air of the type N_xO_y depending on the composition mentioned be assumed for it, the density of air would be far greater than the actual value. Thus the compound character of air is disproved.

(6) The ingredients of a mechanical mixture can be separated by easy mechanical means of separation like diffusion, distillation, vaporisation, etc., but the components of a chemical compound cannot be so separated.

The constituents of air can be separated

(*a*) *By diffusion*: When air is passed through a porous tube and then the tube be closed at both ends, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen through the porous tube and the residual air left in the tube will be found to be richer in oxygen than ordinary air. Had air been a chemical compound, no such separation of the constituents would have been possible.

(*b*) *By vaporisation* : When liquid air is allowed to evaporate, the boiling point increases from—192°C. progressively. Further, the gas which comes out first is richer in nitrogen than the gas which comes out afterwards. Hence liquid air is to be considered as a mixture of two liquids, liquid nitrogen and liquid oxygen, and it may be presumed that atmospheric air is also a mixture of the gases, nitrogen and oxygen.

(c) *By solution in water* : If air be shaken with water, a part of it goes into solution, and the dissolved gas can be expelled by boiling. It has been found that the air thus recovered from solution is very much richer in oxygen than ordinary air. Thus a partial separation of the ingredients of air by solution in water followed by subsequent heating, *i.e.*, by easy mechanical means, is possible.

Air is thus proved to be a mechanical mixture.

Now any single argument given in the above discussion may not be considered sufficient, but the arguments taken all together prove completely that air is a mechanical mixture, and *not a chemical compound*, of nitrogen and oxygen.

But nitrous oxide does not satisfy any of the tests applied in the case of air for proving its mixture character. On the other hand, the characteristics of definite chemical compound of nitrogen and oxygen are present in nitrous oxide. Thus,

(1) Oxygen in nitrous oxide cannot be removed by absorption with alkaline pyrogallate, nor the oxygen in it produces brown fumes with nitric oxide (a characteristic of free oxygen).

(2) Oxygen present in nitrous oxide cannot be separated by easy mechanical means as mentioned in the case of separation of oxygen from air.

(3) Whatever may be the source of nitrous oxide, it has always the same composition by weight, viz., 7 parts by weight of nitrogen combined with 4 parts by weight of oxygen.

(4) In the formation of nitrous oxide from nitrogen and oxygen, heat is absorbed and heat is given up during its decomposition.

(5) The volumetric composition of the gas nitrous oxide can be utilised for deriving its formula and its density agrees with the formula so derived.

(6) In nitrous oxide 2 volumes of nitrogen combining with 1 volume of oxygen give rise to 2 volumes of nitrous oxide but in air 4 volumes of nitrogen and 1 volume of oxygen give rise exactly to 5 volumes of air.

For determining which cylinder contains which gas, push the cover plates of the cylinders a little. The cylinder in which brown fumes are visible contains nitric oxide. Then bring each of the other two cylinders mouth to mouth with the cylinder containing nitric oxide and push the cover plates aside. That cylinder, the contents of which produce copious brown fumes with nitric oxide, contains air and the remaining one contains nitrous oxide.

Nitric oxide is first converted into nitrogen peroxide by mixing with pure oxygen or air.

$$2NO + O_2 = 2NO_2.$$

This nitrogen peroxide, with hot water, gives nitric acid,

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

When this nitric acid mixed with an equal volume of water is treated with copper turnings, nitric oxide is evolved and can be collected, after allowing the brown fumes of NO_2 to escape, by displacement of water.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

When nitric oxide is passed into a solution of ferrous sulphate which is faintly green in colour, the colour of the solution turns brown, due to the formation of a loose compound. $FeSO_4.NO$.

$$FeSO_4 + NO = FeSO_4.NO.$$

Q. 4. *Name the principal ores of copper with their formulae. How is the metal extracted from its sulphide ore and how is it refined? Explain the chemical reactions involved in the different stages of the process.*

State the uses of the metal and its important alloys.

Starting from copper, describe how you would prepare a sample of cuprous chloride.

Ans. The principal ores of copper are :—

(1) Ruby ore, red copper ore or Cuprite, Cu_2O.

(2) Tenorite, CuO.

(3) Copper glance, Cu_2S.
(4) Covellite or indigo copper, CuS.
(5) Copper pyrites, Cu_2S, Fe_2S_3 or $CuFeS_2$.
(6) Bornite or purple copper ore, $3Cu_2S, Fe_2S_3$ or Cu_3FeS_3.
(7) Malachite, $CuCO_3,Cu(OH)_2$.
(8) Azurite, $2CuCO_3, Cu(OH)_2$.

Extraction of copper from its sulphide ores, viz., from copper pyrites which is the abundant sulphide ore, is carried out in the following way :—

(1) The sulphide ores of copper in general contain on an average 4 to 5 per cent. of copper. Hence a preliminary concentration of the ores is necessary and is carried out by *oil floatation process*. For this purpose the ore is first crushed and finely powdered. The powdered ore is next added to water containing a little pine oil and lime, and the mixture churned by blowing air through it. By this operation a froth is formed and comes to the top, carrying along with it the particles of copper ore, which are preferentially wetted by oil ; sand and other impurities are left in the bottom of the vessel, these being preferentially wetted by water. The froth is collected by skimming and allowed to settle. The ore now contains 30 to 35 per cent. of copper.

(2) The concentrated ore is next roasted in a multiple hearth furnace, the ore descending from hearth to hearth during roasting operation. Sulphur present in the ore is thus partially burnt out, forming SO_2 and the metals are partially oxidised.

$$Cu_2S, Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S, Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2.$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$

The last reaction occurs only to a very small extent.

(3) The roasted ore is then mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when a little quantity of Cu_2O formed in the previous operation reacts with iron sulphide present giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced in the previous operation reacts with sand or silica, giving slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed in molten condition from above the mixture of cuprous and ferrous sulphides, known as *copper matte* or simply *matte.*

(4) The molten matte is then directly run into a Bessemer type converter with a little silica and a blast of air is introduced through tuyeres set at the sides of the converter a little above the bottom level. Iron is first oxidised here to FeO which combines with silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued. Cu_2S then begins to oxidise to Cu_2O and when about two-third of Cu_2S is converted into Cu_2O, unchanged Cu_2S and Cu_2O react with the production of metallic copper.

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The slag is removed, the blast stopped and the converter tilted to pour off molten copper. On cooling this copper assumes a blistered appearance due to escape of SO_2 and is known as "blistered copper".

(5) Blistered copper is refined by melting it down on the hearth of a reverberatory furnace when impurities like sulphur, lead, iron etc, are oxidised. Some of the products of oxidation escape as gas, others form slag with the furnace lining of silica, which is removed. Next the metal begins to oxidise. Anthracite coal in powder form is then sprinkled on the molten metal and the mass is stirred with logs of green wood. When the copper attains the requisite *tough*-pitch, it is poured out. Thermally refined copper is 99·9% pure.

Further purification of copper can be effected by electrolysis. Thick sheets of impure copper are suspended from a metal rod in a bath of $CuSO_4$ solution, *acidified* with 15% of sulphuric acid, and taken in an wooden vessel lined with lead. Thin plates of pure copper are suspended from another metal rod and are dipped in the same bath in such a fashion that these are inserted alternately between the thick sheets. The rod carrying the thick slabs is connected to the positive pole of a battery, thus making the thick slabs to function as anodes ; the rod carrying the thin sheets of pure copper is connected to the negative pole of the same battery and thereby the thin sheets of pure copper are made to function as cathodes. On passing electric current through the bath of copper sulphate, copper ions pass into solution from thick sheets gradually and are deposited as pure metallic copper on thin sheets after neutralisation of charge on them. Impurities present either pass into solution or are deposited at the bottom of the bath near the anodes as *anode mud.* Copper, thus obtained as a deposit on the cathode, is 99·99% pure.

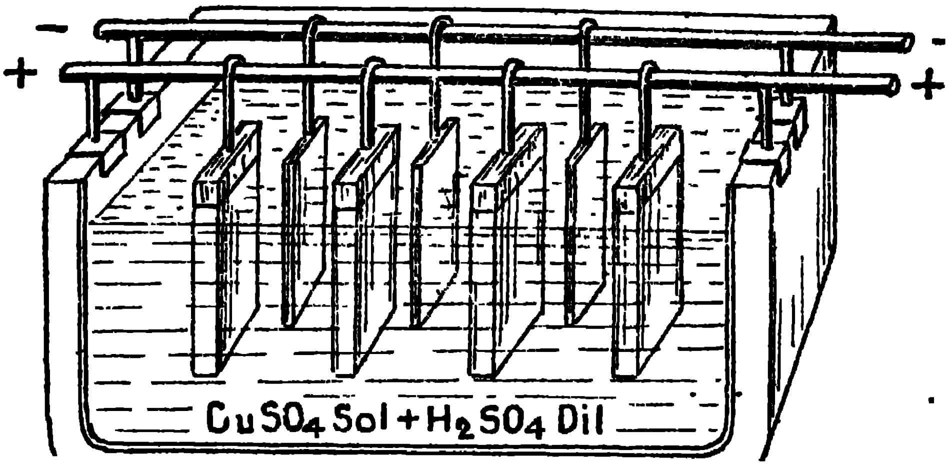


Fig. 74

Uses of copper :—Copper is largely used in electric industry, in electro-typing, for cables and wires for conveying electric current, and in setting up voltaic cells ; it is also used in the preparation of household utensils, for coinage and for the preparation of alloys, like brass, bronze, German silver, etc.

Brass is one important alloy of copper and zinc. It is used for preparing house-hold utensils, cartridge cases and in machinery parts. *Bronze* is another alloy of copper with tin. It is used for making medals, statues, etc. Alloyed with a little amount of zinc, bronze is used in coinage. *German-silver* is an alloy of copper, zinc and nickel. It is used for preparation of cheap ornaments as also utensils for every-day use.

A portion of the copper supplied in the form of copper turnings is taken, dissolved in nitric acid, the solution is evaporated to dryness and the residue strongly ignited when cupric oxide is produced.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

This black residue of cupric oxide is taken in a flask and excess of concentrated HCl is added to it. Then the remaining portion of copper turnings is added to it and the mixture boiled. When the reactions are over, the liquid portion is poured into a large volume of water when a white precipitate of cuprous chloride is obtained.

$$CuO + 2HCl = CuCl_2 + H_2O$$
$$Cu + CuCl_2 = Cu_2Cl_2.$$

Q. 5. *Describe the preparation and properties of the following substances, and state their uses :—*

(a) Plaster of Paris, (b) Bleaching powder, (c) Calomel, (d) Corrosive sublimate.

Ans. (a) **Plaster of Paris** is prepared by heating gypsum, $CaSO_4, 2H_2O$, in kiln or oven to a temperature not exceeding 120°C. out of contact with carbonaceous fuel. The above two precautions are to be essentially complied with, otherwise (1) gypsum becomes *dead burnt* and fails to set with water, and (2) in contact with carbonaceous fuel, it will be reduced to calcium sulphide, CaS.

$$2(CaSO_4, 2H_2O) = (CaSO_4)_2, H_2O + 3H_2O.$$

Properties :—Plaster of Paris is a *white powder*. It forms a hard mass with water ; this phenomenon is known as setting of plaster of Paris. It is due to rehydration and reconversion into gypsum of Plaster of Paris.

$$(CaSO_4)_2, H_2O + 3H_2O = 2(CaSO_4, 2H_2O)$$

Uses :—Plaster of Paris is used for making *moulds* in pottery work and other purposes ; in surgical bandges ; as a cement in ornamental castings and in the preparation of busts and statues.

(b) **Bleaching powder** is prepared by the action of chlorine on dry slaked lime. Slaked lime, containing not more than 4% of water, is spread upon the wooden floor of a chamber provided with glass doors and windows. There are wooden stirrers, fitted into the chamber, by means of which the lime may be raked from time to time. There is also a fan arrangement in the chamber by means of which lime may be dusted in. Dry chlorine, freed from HCl and CO_2, is passed into the chamber by an inlet pipe. The gas is at first absorbed by lime rapidly and when it slackens down, lime is raked with the wooden stirrers. The temperature is kept below 40°C. by circulating calcium chloride solution through pipes set in the floor of the chamber. The lime is left in contact with chlorine for about 24 hours. At the end of the operation powdered slaked lime is dusted inside the chamber by the fan arrangement in order to absorb the last trace of chlorine left in excess. Bleaching powder is next taken out by removing the wooden planks from the floor and packed in barrels.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O,$$

Properties of bleaching powder.—

Bleaching powder is a white solid with the smell of dilute chlorine. Acids, including even the weak carbonic acid, liberate chlorine from bleaching powder ; thus with HCl, the following reaction takes place.

$$Ca(OCl)Cl + 2HCl = CaCl_2 + Cl_2 + H_2O.$$

In water solution, it breaks down into a mixture of $CaCl_2$ and $Ca(OCl)_2$.

$$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2.$$

All good bleaching powder contains a little free lime.

Uses :—Bleaching powder is used for bleaching fabrics and as a disinfectant.

(c) **Calomel** or mercurous chloride is prepared by heating an intimate mixture of mercuric chloride and metallic mercury in an almost closed vessel. Mercurous chloride vaporises and is condensed in the upper cooler part of the vessel in the solid state. The sublimate so formed is collected by scraping and is repeatedly boiled with water to remove any mercuric chloride that also comes over as vapour and collects along with the mercurous chloride, the residue of mercurous chloride is filtered, and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Properties :—Mercurous chloride or calomel is a white powder, amorphous in character and without any taste. It is insoluble in water and in dilute acids. It is soluble only in aqua regia, by which it is changed to mercuric chloride. On heating it sublimes unchanged. On adding ammonia to it, it turns black, possibly due to separation of metallic Hg in a fine state of division and at the same time amidomercuric chloride, NH_2HgCl, is produced.

$$Hg_2Cl_2 + NH_3 = NH_2HgCl + HCl + Hg.$$

Uses.—Calomel is used in medicine as a purgative.

(d) **Corrosive sublimate** of Mercuric chloride can be prepared by dissolving either mercury or calomel in aqua regia, filtering the solution so obtained and then crystallising the solution by evaporation. It is usually obtained by heating a mixture of mercuric sulphate and sodium chloride (common salt) in long-necked, flat-bottomed flasks on a sand bath. A little manganese dioxide is added to the mixture in order to prevent the formation of calomel by the action of reducing agent present in commercial common salt.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

After the reaction is over the flasks are cooled and then broken in order to collect the cake of mercuric chloride condensed on the upper part of the flasks. The cakes are dissolved in water, filtered and re-crystallised from solution for getting pure product.

Properties :—Corrosive sublimate is a white, crystalline solid, the crystals being needle-shaped. It is soluble in water, but its solubility in ether or in alcohol is greater than it is in water. It is extremely poisonous. Egg albumen (white portion of eggs) forms an insoluble compound with mercuric chloride, and is, therefore, utilised as an antidote in case of mercuric chloride being inadvertently swallowed. It is reduced by stannous chloride first into mercurous chloride and then, with more stannous chloride, into metallic mercury.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

On adding ammonia to mercuric chloride, a white precipitate called *infusible white precipitate*—of amidomercuric chloride (NH_2HgCl) is formed.

$$NH_3 + HgCl_2 = NH_2HgCl + HCl.$$

On adding potassium iodide solution to mercuric chloride solution, at first a red precipitate of mercuric iodide is formed, but the red precipitate dissolves to a colourless solution by adding an excess of potassium iodide solution.

$$2KI + HgCl_2 = 2KCl + HgI_2$$
$$2KI + HgI_2 = K_2HgI_4.$$

Uses :—Corrosive sublimate is used in medicine as an antiseptic. It is also employed in taxidermy for dressing skins, furs, etc.

Q. 6. *Write what you know about* **any one** *of the following* :—

(*a*) *Hardness of water*, (*b*) *rusting of iron*, (*c*) *oxidation and reduction*, (*d*) *indestructibility of matter.*

Ans. (*a*) Hardness of water means the difficulty encountered in certain samples of water in producing lather with soap. With samples of such hard water, lather with soap is produced after much soap is consumed, and so with such water there is much wastage of soap in cleansing operation. Hardness of water is due to the presence of soluble calcium and magnesium salts in solution. When the hardness is due to the presence of bicarbonates of calcium and magnesium in solution, it is called 'temporary hardness' ; but when hardness is due to the presence of chlorides and sulphates of calcium and magnesium in solution, it is called 'parmanent hardness' of water. For washing of clothes, therefore, hardness of water is to be removed and this operation of removing hardness of water is known as 'softening of water.' At present softening of water for industrial purposes is mostly carried out by Gan's Permutit Process, by which both types of hardness can be removed. Permutits are aluminosilicates of sodium which have the capacity of exchanging bases and hence by filtering hard water through beds of permutit, calcium and magnesium in the salts present in such water are replaced by sodium and the sodium compounds are innocuous from the standpoint of washing with soap.

(*b*) A piece of iron, when exposed to moist air for a time, is found to be covered with loose, non-coherent, easily detachable, brown coating called *rust.* The process of formation of the rust is called *rusting.* The rust is found on analysis to be chiefly hydrated ferric oxide of the formula $2Fe_2O_3, 3H_2O$. But along with the hydrated ferric oxide rust contains ferrous carbonate and hydrated ferrous oxide. The composition of rust depends upon its age and hydrated ferric oxide predominates in the long run.

Both air and water are necessary for the formation of rust. Several theories have been advanced from time to time to explain the rusting phenomenon.

The first theory to be stated is that iron rusts due to the oxidation of iron through the intermediate formation of ferrous carbonate by the action of atmospheric CO_2 and moisture.

$$Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

The other theory suggests that CO_2 is not essential for rusting to take place. But rusting occurs through the agency of H_2O_2 produced by the simultaneous attack of moisture and oxygen on iron.

$$Fe + O_2 + H_2O = FeO + H_2O_2$$
$$2FeO + H_2O_2 = Fe_2O_3 + H_2O.$$

In support of this theory it is stated that though hydrogen peroxide cannot detected in the solution, yet substances which destroy H_2O_2 prevent rusting.

Yet another theory stated about rusting is that rusting occurs due to voltaic action, impurities present in iron setting up a voltaic cell in contact with water containing dissolved oxygen. In support of this theory it may be stated that very pure iron does not rust when exposed to ordinary moist air.

Rusting of iron is a serious problem in view of the fact that a great loss is incurred by mankind due to this transformation of iron to hydrated ferric oxide which scales off readily from the surface of iron. Hence attempt is made all over the world to prevent this rusting of iron. Several processes are in operation, viz. (a) covering of the iron surface with paints, like Al powder, red lead, etc., coal tar, pitch, etc. ; (b) covering the metal surface with a layer of Fe_3O_4 by blowing steam over the red hot metal ; (c) *galvanising* with zinc, *tinning* and *calorising* (*i.e.* coating with aluminium oxide on the surface followed by aluminium metal coating in the interior.)

(*c*) **Oxidation** is the process which increases the proportion of oxygen or of an equivalent electro-negative element or radical in an element or a compound, or diminishes the proportion of hydrogen or of an electro-positive element or radical in a compound.

Reduction is just the reverse operation to oxidation. Thus, reduction is the process which increases the proportion of hydrogen or of an electro-positive element or radical in an element or a compound, or diminishes the proportion of oxygen or of an equivalent electro-negative element or radical in a compound.

Illustration of the phenomenon of oxidation :—

(i) When sulphur is burnt in oxygen, it is *oxidised* to sulphur dioxide, by adding up oxygen :

$$S + O_2 = SO_2.$$

(ii) When iron is heated in a stream of chlorine gas, it is oxidised to ferric chloride, by adding up an electro-negative element, chlorine, to itself :—

$$2Fe + 3Cl_2 = 2FeCl_3.$$

(iii) When hydrochloric acid is heated with manganese dioxide, it is oxidised to chlorine by removal of hydrogen :—

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

(iv) When potassium iodide solution is treated with hydrogen peroxide, it is oxidised to iodine by removal of the electro-positive element potassium :—

$$2KI + H_2O_2 = 2KOH + I_2$$

Illustrations of the phenomenon of reduction :—

(i) When hydrogen gas is passed over heated copper oxide (black), CuO is reduced to metallic copper (red) by removal of oxygen :—

$$CuO + H_2 = Cu + H_2O.$$

(ii) When ferric chloride solution (yellow) is treated with granulated zinc and hydrochloric acid, ferric chloride is reduced to ferrous chloride (solution colourless) by nascent hydrogen by the removal of a certain proportion of the electro-negative element chlorine :—

$$FeCl_3 + H = FeCl_2 + HCl.$$

(iii) When sulphuretted hydrogen is passed into iodine suspended in water, iodine is reduced to hydroiodic and by addition of hydrogen :—

$$H_2S + I_2 = 2HI + S.$$

(iv) when mercury is triturated with iodine in a mortar, iodine is reduced to mercurous and mercuric iodides, by the addition of the eletro-positive element mercury :—

$$2Hg + I_2 = Hg_2I_2$$
$$Hg + I_2 = HgI_2.$$

Among inorganic compounds, oxidation usually denotes an increase in the active valency of the central atom, as for example, when ferrous chloride is oxidised to ferric chloride, or stannous chloride is oxidised to stannic chloride.

$$Fe^{+2}Cl_2 \xrightarrow{Cl_2} Fe^{+3}Cl_3$$
$$Sn^{+2}Cl_2 \xrightarrow{Cl_2} Sn^{+4}Cl_4$$

From ionic standpoint, if we take into consideration the reaction

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2\ FeCl_2,$$

it can be represented as

$$2\ Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised by the loss of two electrous which have passed to the two ferric ions, reducing them to the ferrous state.

Hence, *oxidation* may be defined as a *loss of electrons* and *reduction* as a *gain of electrons.*

Moreover, it must also be observed that oxidation and reduction take place simultaneously in a system. Whenever a substance is oxidised, another one is reduced. Thus, when stannous chloride solution is added to a solution of mercuric chloride, a white precipitate of mercurous chloride is obtained. Here mercuric chloride is reduced to mercurous chloride, but at the same time stannous chloride is oxidised to stannic chloride.

$$2\ HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

(a) **Indestructibility of matter** is now accepted as a law of nature and on the basis of this law the whole superstructure of chemistry is built up. The law has been established from a series of experiments performed from the time of Lavoisier who introduced the use of balance in the study of chemistry. The law is stated as follows :—

Matter is indestructible ; it can neither be created nor destroyed by any reaction whatsoever, but can be transformed from one form into the other. So the total quantity of matter in every chemical change is exactly the same after the change as the total quantity of matter before the change.

The truth of the above statement can be seen by the famous **charcoal experiment.** A round-bottomed flask is provided with a tightly-fitting rubber-cork, through which two stout copper wires are fitted. One of the copper wires is fitted with a copper spoon. A piece of charcoal is placed on the spoon and a very thin platinum wire, joining the two copper wires, is wound round the piece of charcoal. The cork with the fitting is removed and the flask is next filled with oxygen by the displacement of air. The cork is then replaced and is tightly fitted to the mouth of the flask. The whole apparatus is then carefully weighed in a chemical balance. Electric current is next passed through the platinum wire by connecting the copper wires to the terminals of a battery. The thin platinum wire becomes red hot by the passage of the current and thereby the piece of charcoal is ignited and burns away to carbon dioxide gas. At the end of the reaction, the whole apparatus is allowed to cool and weighed again carefully. It is found that though the piece of charcoal has almost completely disappeared (a little ash being left behind) and is practically lost, the weight of the apparatus has remained *unchanged.* This proves that though charcoal has undergone a chemical change with apparent loss of matter, yet nothing is lost.

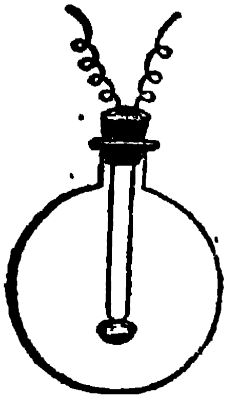


Fig. 75

The best experiments for establishing the truth of the Law of indestructibility of Matter are those carried out by Landolt for 15 years till 1908.

In one of his experiments Landolt took solutions of ferrous sulphate and silver sulphate in two different arms of a H-shaped tube as shown in the figure. These two substances were chosen because they would react together without the production of *much* heat. The ends of the H-tube were next sealed in order that there might not be any mechanical loss of materials. The tube was next weighed accurately in a sensitive balance, using another such H-tube as a counterpoise. Then the two solutions were carefully mixed together by tilting the tube. A chemical reaction occurred and metallic silver was deposited due to the reducing action of ferrous sulphate.

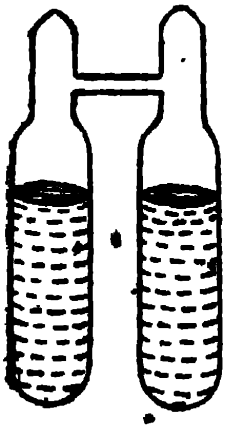


Fig. 76

$$Ag_2SO_4 + 2FeSO_4 = Fe_2(SO_4)_3 + 2Ag.$$

After the reaction was over, the tube was allowed to cool for some time and then weighed in the same balance by using the same counterpoise. Landolt found that the weight remained practically constant, though there was an apparent creation of matter.

It is clearly seen from the experiment described that there has been no destruction or creation of Matter.

✓Q. 7. *Explain, giving equations, what happens when :—*

(*a*) *Hydrogen sulphide is passed into a suspension of iodine in water ;*

(*b*) *ammonia is added to a solution of silver nitrate :*

(*c*) *sulphur is heated with strong sulphuric acid ;*

(*d*) *zinc is added to a solution of copper sulphate ;*

(*e*) *green vitriol is gradually heated to redness in a tube.*

Ans. (*a*) When hydrogen sulphide is passed into a suspension of iodine in water, hydroiodic acid is formed in solution and sulphur separates. The colour of the mixture becomes yellowish-white due to separation of sulphur.

$$H_2S + I_2 = 2HI + S.$$

(*b*) When ammonia is added to a solution of silver nitrate, a transient white precipitate appears and disappears very soon and a solution is obtained, containing silver ammine nitrate, a complex salt. The transient white ppt. is of silver oxide.

$$2AgNO_3 + 2NH_4OH = Ag_2O + 2NH_4NO_3 + H_2O$$
$$AgNO_3 + 2NH_4OH = [Ag(NH_3)_2]NO_3 + 2H_2O.$$

(c) When sulphur is heated with strong sulphuric acid, sulphur dioxide gas is evolved and suffocating odour of burning sulphur is perceived.

$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$

(d) When zinc is added to a solution of copper sulphate, zinc passes into solution and metallic copper is deposited.

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

(e) When green vitriol, $FeSO_4, 7H_2O$ is gradually heated to redness in a tube, at first water of crystallisation is expelled as water vapour, giving first the mono-hydrate, $FeSO_4, H_2O$. The mono-hydrate, on heating at 300°c. in absence of air, since the heating is conducted in a tube, gives the *anhydrous* salt $FeSO_4$ which is white in colour. At red-heat it decomposes into Fe_2O_3, $SO_3$and SO_2.

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

A brown residue of ferric oxide is left in the tube, sulphur trioxide and sulphur dioxide escaping as gases.

Q. 8. *Starting from iron filings, describe experiments to show that iron forms two series of salts, ferrous and ferric. Where lies the difference between the two types? By what tests would you distinguish between them? Describe how you convert one to the other and vice versa.*

Give equations in support of your answer.

Ans. Take iron filings in a beaker and then add dil. HCl to it. Hydrogen gas is evolved and iron passes into solution. Wait till all the iron filings have dissolved. Then evaporate the solution out of contact with air and crystallise, when crystals of $FeCl_2, 4H_2O$ are obtained.

$$Fe + 2HCl = FeCl_2 + H_2.$$

It is a green crystalline solid soluble in water.

Next dissolve the iron filings in a beaker in aqua regia, a mixture of hydrochloric and nitric acids. Wait till all the iron filings have disappeared. Evaporate the solution to crystallisation, when yellow crystals of ferric chloride $FeCl_3, 6H_2O$ will separate out.

It is a yellow crystalline solid, soluble in water.

Thus two substances are obtained from iron filings, both containing only iron and chlorine as analysis reveals, but one contains 2 atoms of chlorine for every atom of iron whereas the other contains 3 atoms of chlorine for each atom of iron as determined by quantitative analysis by precipitation of their solutions with silver nitrate after removal of iron with ammonia and determination of iron in them by suitable methods. Thus the two series of salts are different.

The difference between the two types lies in the difference in the valency state of iron in the two classes of compounds. In the first type, called the ferrous compounds, iron is bivalent, whereas in the second type, called the ferric compounds, iron is trivalent.

The reagents used for distinguishing between the ferrous and the ferric compounds are potassium ferro cyanide, potassium ferri-cyanide and ammonium thiocyanate.

Potassium ferro-cyanide gives *white* ppt. with ferrous salts when the ferrous compounds are completely free from any ferric compound, otherwise, if oxidation by air has caused a little ferric compound to be formed in the ferrous salt, a light blue ppt. will be produced in that case. With ferric compounds, potassium ferro-cyanide produces a dark blue ppt.

Potassium ferri-cyanide, on the other hand, produces a dark blue ppt. with ferrous compound, and no ppt. but a brown or green coloration only with ferric compounds.

Ammonium thio-cyanate produces no coloration with ferrous salts when absolutely pure, but produces a blood-red coloration with ferric compounds.

When a ferrous compound, say ferrous chloride, is treated with an oxidizing agent like aqua regia, it is converted into ferric chloride.

$$HNO_3 + 3HCl = NOCl + 2H_2O + 2Cl \text{ (nascent)}$$

$$FeCl_2 + Cl = FeCl_3.$$

When ferric chloride in hydrochloric acid solution in a boiling state is treated with stannous chloride solution which is a reducing agent, it is reduced to ferrous chloride.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

1951

FIRST PAPER

Q. 1. *State and illustrate the law of Multiple Proportions and show how it follows from the Atomic Theory.*

Two oxides of a metal, M, when heated to a constant weight in a current of hydrogen gave 0·12585 gm. and 0·2264 gm. of water respectively per gram of the oxide used. If the formula for the latter be given by MO, find that for the other.

Ans. *When two elements combine to form two or more different compounds, the weights of one of the elements which combine with a constant weight of the other bear a simple ratio to one another.* The Law of Multiple Proportions is stated as above; the term *simple ratio* indicating that the ratio is capable of being expressed by simple whole numbers.

The law is illustrated by taking into consideration the two compounds formed by two elements carbon and oxygen, *viz.*, carbon monoxide and carbon dioxide.

In carbon monoxide, 12 parts by weight of carbon is in combination with 16 parts by weight of oxygen.

In carbon dioxide, 12 parts by weight of carbon is in combination with 32 parts by weight of oxygen.

Therefore the different parts by weight of oxygen, *viz.*, 16 and 32, which combine with a constant weight of carbon (*viz.* 12 parts by weight) are in the ratio of 16 : 32, *i.e.*, of 1 : 2—which is a simple ratio.

The law can be deduced from the famous Atomic Theory of Dalton. The following are the postulates of the Atomic Theory.

(1) Matter is discrete and is composed of minute particles called *atoms*, which is incapable of further subdivision. Atoms can neither be created nor destroyed by any chemical process.

(2) Atoms of the *same* element are similar to one another in all respects and are equal in weight.

(3) Atoms of different elements have different weights and different properties.

(4) Chemical combination between two or more elements takes place by the *juxtaposition* of the atoms of those elements in simple numerical proportions, *viz.* 1 : 1, 1 : 2, 2 : 3, 3 : 2 *etc.*

(4) The combining weights of the elements represent the combining weights of the atoms.

From the above postulates of the Atomic theory, the Law of Multiple Proportions is deduced in the following way :

Let the two elements A and B combine chemically to produce more than two compounds ; and let us suppose that the *simplest* of these compounds contains 1 atom of A combined with 1 atom of B in a molecule of it. Its formula, therefore, is AB. Since atoms are indivisible and compounds are formed by the juxtaposition of atoms in simple numerical proportions (Dalton's Atomic Theory), 1 or more atoms of A will combine with 2 or more atoms of B, or 1 or more atoms of B will combine with 2 or more atoms of A to produce the other compounds of A and B. Let us suppose that the formula of a second compound of A and B be AB_2 and that of a third compound, A_2B_3. Let us assume that the atomic weights of A and B are x and y respectively. Then we find that,

(*i*) in the compound AB,

x parts by weight of A are in combination with y parts by weight of B ; .

(*ii*) in the compound AB_2

x parts by weight of A are in combination with $2y$ parts by weight of B ;

(*iii*) in the compound A_2B_3,

$2x$ parts by weight of A are in combination with $3y$ parts by weight of B ; that is,

x parts by weight of A are in combination with $\frac{3y}{2}$ parts by weight of B.

Therefore, the weights of B which are in combination with a constant weight of A, *viz.*, x, are in the ratio

$$y : 2y : \frac{3y}{2} \quad \text{or} \quad 1 : 2 : \frac{3}{2} \quad \text{or} \quad 2 : 4 : 3,$$

which is a simple ratio. Hence we see that the Law of Multiple Proportions follows from the Atomic Theory.

I. 0·12585 gm. of water contains $0·12585 \times \frac{8}{9}$ gm. or 0·1116 gm. of oxygen. Since this oxygen comes from 1 gm. of the oxide of the metal, $(1 - 0·1116)$ gm, or 0·8884 gm. of the metal has combined with 0·1116 gm. of oxygen to form this oxide. Hence in this oxide the ratio of the weights of oxygen : metal is as 1 : 8 app.

II. 0·2264 gm. of water contains $0·2264 \times \frac{8}{9}$ gm. or 0·2012 gm. of oxygen. Since this amount of oxygen comes from 1 gm. of the oxide of the metal, $(1 - 0·2012)$ gm. or 0·7988 gm. of the metal has combined with 0·2012 gm. of oxygen to form this oxide. Hence in this oxide the ratio of the weights of oxygen : metal is as 1 : 4 app.

Now, it is given that the formula of the second oxide can be written as MO. Now in the second oxide 16 parts by weight of oxygen is in combination with 64 parts by weight of the metal. But in the first oxide 16 parts by weight of oxygen is in combination with 128 parts by weight of the metal. Thus, 64 parts by weight of the metal represents 1 atom of the metal and therefore 128 parts by weight of the metal stands for 2 atoms of the metal. In both cases 16 parts by weight of oxygen stands for 1 atom of oxygen. Hence the formula for the first oxide can be written as M_2O.

Q. 2. *Describe experiments by which you can determine the volumetric composition of steam. How would you deduce therefrom its molecular formula ?*

Both air and steam are known to contain a common constituent. What is the evidence that in one it is chemically combined while in the other it merely forms part of a mixture ?

Ans. There is only experiment to determine the volumetric composition of steam. Composition of water can be determined experimentally by the electrolysis of acidulated water in a water voltameter and collecting the gases evolved at the anode and at the cathode separately in graduated tubes. It will be found that the volume of the gas collecting in the tube placed over the cathode is double the volume of the gas collecting in the tube placed above the anode. Also it can be proved by usual tests that the gas collecting over the cathode is hydrogen and that collecting over the anode is oxygen. Thus it is established that 2 volumes of hydrogen combine with 1 volume of oxygen to produce water.

The volumetric composition of steam is determined by Hofmann's experiment. The apparatus consists of a U-shaped eudiometer tube one limb of which is closed and graduated. Near the closed end, two platinum wires are sealed into the glass, so that with their help gases inside the tube can be fired by passing a spark. The closed limb is surrounded by a wider tube to serve as a jacket, through which amyl alcohol vapour (B. P. 132°C.) can be circulated when required. The other limb of the eudiometer tube is open and is provided with a side-cock near the bottom.

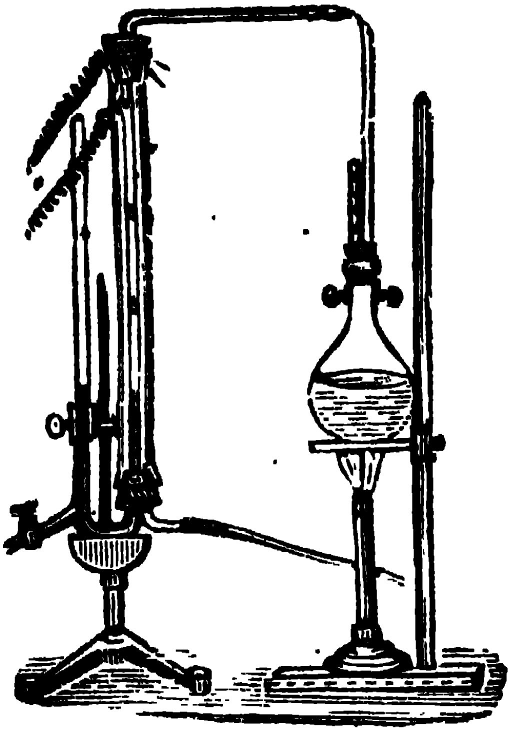


Fig. 77

In performing the experiment, the closed limb of the eudiometer tube is first filled up with mercury and then a mixture of 2 volumes of hydrogen and 1 volume of oxygen (obtained by the electrolysis of acidulated water, collecting the gases evolved at the anode and the cathode together and known as *detonating gas*), dried by passing through conc. H_2SO_4 was introduced into it by the displacement of mercury. Vapour of amyl alcohol, obtained by boiling amyl alcohol in a flask, is then passed through a tube, as shown in the figure, the tube being attached to the top of the jacket. This passage of amyl alcohol vapour through the jacket tube is continued upto the end of the experiment. The amyl-alcohol vapour, passing out of the jacket-tube by the lower exit tube, is led to a condenser. After some time, when the temperature of the mixed gases becomes constant, the mercury level in both the limbs is adjusted to the same height and the volume of the mixture is carefully noted. Some mercury is then run out by opening the side-cock to reduce the pressure, the open end is next closed by the thumb and a single electric spark is passed through the gas mixture by connecting the two platinum wires sealed to the closed limb to the terminals of an induction coil. Hydrogen and oxygen combine with explosion to produce steam. Mercury is now poured in through the open limb in order to adjust its level in both the limbs to the same height. The volume is then read off carefully.

It is found that the volume of steam produced is exactly *two-thirds* of the volume of the mixture of hydrogen and oxygen taken.

From the experiment described we come to know that also in the case of steam, as in the case of water, 2 volumes of hydrogen combine with 1 volume of oxygen and that 2 vols. of steam are produced thereby.

The molecular formula of steam can be deduced from the above experimental result by the application of Avogadro's hypothesis.

Let "*n*" be the number of molecules present in 1 volume of each gas.

Then, by Avogadro's hypothesis, we get $2n$ molecules of hydrogen combine with n molecules of oxygen to produce $2n$ molecules of steam.

Or, 2 molecules of hydrogen combine with 1 molecule of oxygen to produce 2 molecules of steam.

Since hydrogen molecules as also oxygen molecules are diatomic (—Deduction from Avogadro's hypothesis), 4 atoms of hydrogen combine with 2 atoms of oxygen to produce 2 molecules of steam; or, 2 atoms of hydrogen combine with 1 atom of oxygen to produce 1 molecule of steam.

Hence, the molecular formula for steam is H_2O. This formula for steam is confirmed by the determination of its vapour density, which is found to be 9. So the molecular weight of steam is 18 and this tallies with its molecular formula H_2O.

The common constituent of air and steam is oxygen. In air, oxygen is present in the free state forming a part of a mixture with nitrogen. This is proved by the following facts :—

(1) The properties of oxygen are found to be present in air, *viz.*, its capacity to support combustion, though modified to a certain extent due to admixture with the inert gas nitrogen, is

found to be present in air. Also free oxygen is known to be absorbed completely by alkaline pyrogallate giving a brown solution ; this is also found to occur with air, oxygen being completely removed from it by shaking with alkaline pyrogallate giving a brown solution.

(2) Separation of oxygen from nitrogen present in air can be carried out by easy mechanical means, *viz.*, by shaking with water air dissolves and by boiling such solution the air that is expelled is found to be richer in oxygen than ordinary air. Thus, a partial separation of oxygen from nitrogen is effected. Also by fractional evaporation of liquid air, nitrogen can first be evaporated away and the oxygen is obtained towards the end of the operation. Also by diffusion a partial separation of oxygen from nitrogen can be carried out. nitrogen passing out through the porous septum at a little greater rate than oxygen and oxygen in a little greater proportion than nitrogen being left behind in the vessel. So partial separation only occurs in this way. Had air been a chemical compound, such separation of its constituents would not have been possible.

On the other hand, water is a chemical compound of oxygen and hydrogen. So all the individual properties of oxygen are found to be absent in it. Neither can oxygen present there support combustion nor can it be extracted by alkaline pyrogallate as in the case of air. Also easy separation by mechanical means of oxygen from hydrogen cannot be effected here.

Q. 2. *Alternative. Both air and nitrous oxide contain both oxygen and nitrogen. How would you prove that in one they are chemically combined, while in the other they form a mechanical mixture ?*

Describe how you would determine the composition of nitrous oxide by volume and deduce its molecular formula therefrom.

Ans. Air is a mechanical mixture of nitrogen and oxygen, whereas nitrous oxide is a chemical compound of nitrogen and oxygen.

The following are the considerations from which it is deduced that air is a mechanical mixture of oxygen and nitrogen.

(1) In air, the properties of its ingredients, *viz.*, of nitrogen and oxygen, are found to be present in tact ; for example, the

characteristic properties of oxygen of supporting combustion, of forming brown fumes with nitric oxide and of being absorbed by alkaline pyrogallate, are all found in air. Only due to dilution with nitrogen, oxygen does not rekindle a glowing chip of wood here and so this property of supporting combustion vigorously is somewhat masked. Again, after the removal of oxygen by alkaline pyrogallate or ammoniacal cuprous chloride, the remaining gas shows all the properties of nitrogen.

From this behaviour we conclude that air is a mechanical mixture of nitrogen and oxygen.

(2) Slight variations are noticed in the composition of air by weight, when it is collected from different localities and in different parts of the year from the same locality. But even the slightest variation in composition is not to be found, if air would have been a chemical compound.

Air is therefore considered to be a mixture of oxygen and nitrogen.

(3) In combination of gases with the formation of their chemical compounds, there is always a heat-change, and very often a change in volume is also observed. But when 1 volume of oxygen is mixed with 4 volumes of nitrogen, there is neither any heat-change, nor there is any change in volume ; yet the mixture behaves in every way as ordinary air.

Thus, air is proved to be a mechanical mixture of oxygen and nitrogen.

(4) The density and other physical properties of air are average of these properties of its constituents, *viz.*, oxygen and nitrogen, in the proportion in which they are present in air. Thus, the density of air, calculated on the mixture rule, is found to tally with the actual density of air. For example, considering air to be a mixture of nitrogen and oxygen in the proportion of 4 : 1 by volume approximately, the calculated density will be $\frac{4 \times 14 + 1 \times 16}{5} = \frac{72}{5} = 14{\cdot}4$, the actual determined density of air.

Therefore, air is nothing but a mechanical mixture of nitrogen and oxygen.

(5) The composition of air by weight (77 per cent. of

nitrogen with 23 per cent. of oxygen) is such that no simple formula can be assigned to it (77 parts by weight of nitrogen can stand for 5½ atoms of nitrogen and 23 parts by weight of oxygen can stand for 1·4375 atoms of oxygen). Also five oxides of nitrogen known follow the Law of Multiple proportions, but here no such law is found to be applicable.

Therefore, air is considered to be a mechanical mixture of nitrogen and oxygen.

(6) The last and the most crucial test for settling the fact that air is a mechanical mixture, is the easy mechanical separation of the constituents of air. The constituents of air can be separated.

(*a*) *by diffusion* :—When air is passed through a porous tube, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen and the residue left is found to be richer in oxygen than ordinary air. Had air been a chemical compound, no such separation of the constituents would have been possible.

(*b*) *by fractional evaporation of liquid air* :—When liquid air (b. pt.—190°C.) is allowed to evaporate, the boiling point increases progressively. The gas which comes out first is richer in nitrogen than the gas which comes out afterwards. Thus, liquid air is to be considered as a mixture of two liquids, liquid nitrogen and liquid oxygen, and it may be presumed that atmospheric air is also a mixture of the gases, nitrogen and oxygen.

(*c*) *by solution in water* :—If air be shaken with water, a part of it goes into solution and the dissolved gas can be expelled by boiling. It has been found that the air thus recovered from solution is very much richer in oxygen than ordinary air. Thus, a partial separation of the ingredients of air by solution in water followed by subsequent heating, *i.e.*, by easy mechanical means, is possible.

Air is, therefore, to be considered as nothing but a mechanical mixture of nitrogen and oxygen, for the composition of a chemical compound cannot be altered by diffusion, or fractional evaporation, or solution.

Any single argument given in the above discussion may not be considered sufficient, but the arguments, taken all together, prove completely that air is a mechanical mixture, and *not* a *compound* of nitrogen and oxygen.

But nitrous oxide is a definite compound of nitrogen and oxygen. This is established from the following considerations :—

(1) Oxygen can not be removed by absorption with alkaline pyrogallate, nor with ammoniacal cuprous chloride ; moreover, the oxygen in nitrous oxide does not produce brown fumes with nitric oxide (a characteristic of free oxygen).

(2) Whatever may be the source of nitrous oxide, it has always the same composition by weight, *viz.*, 14 parts by weight of nitrogen combined with 8 parts by weight of oxygen.

(3) In the formation of nitrous oxide from nitrogen and oxygen heat is absorbed, and heat is given up during its decomposition. Also 2 volumes of nitrogen combine with 1 volume of oxygen and give rise to 2 volumes of nitrous oxide. Hence there is also a volume change in the formation of nitrous oxide from its elements.

(4) The volumetric composition of nitrous oxide mentioned above can be utilised for determining its formula and its experimentally determined density agrees with that calculated from its formula so derived.

(5) Oxygen present in nitrous oxide cannot be separated by easy mechanical means as mentioned in the case of separation of oxygen from air.

Composition of nitrous oxide by volume and deduction of its molecular formula :—

The volumetric composition of nitrous oxide is determined by the *thumb-tube method.* A thumb-tube is filled with mercury and is inverted over a deep trough of mercury, as shown in the adjoining figure.

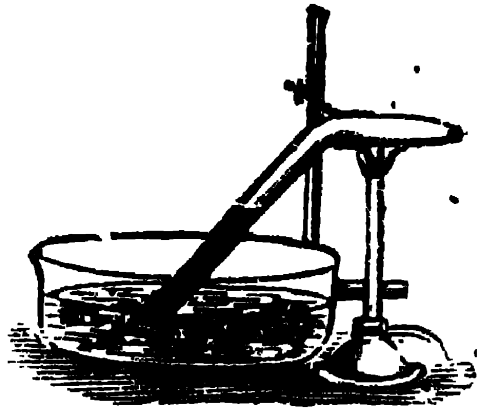


Fig. 78

Nearly half of this thumb tube is filled up with dry nitrous oxide by the displacement of mercury and the position of the mercury level is marked with a rubber band after making the inside and outside level of mercury the same. Next a piece metallic sodium is introduced inside the thumb-tube, by placing it under mercury inside the tube. Then by holding the tube with the hand after closing the open end with the thumb, the piece of sodium is taken to the horizontal part of the tube by a jerking motion given to the tube. The tube is then replaced inside the trough of mercury. Next, the piece of sodium is heated from outside with a Bunsen burner, when it catches fire and combines with all the oxygen of nitrous oxide giving mainly sodium peroxide which is a solid and so occupies negligible volume.

$$2Na + 2N_2O = Na_2O_2 + 2N_2.$$

Nitrogen gas is left behind, as is proved by its inertness, its incapability to turn lime water milky and its complete absorption by heated magnesium. The apparatus is allowed to cool and the level of mercury is adjusted to the same height inside and outside the tube. The mercury level is found to stand exactly at the same place as before. Thus it is proved that nitrous oxide contains its own volume of nitrogen.

Deduction of the molecular formula of nitrous oxide :—

From the above experiment we know that 1 volume of nitrous oxide contains 1 volume of nitrogen. Let "*n*" be the number of molecules present in 1 vol. of nitrous oxide. Then, by Avogadro's hypothesis, *n* molecules of nitrous oxide contain *n* molecules of nitrogen. Therefore, 1 molecule of nitrous oxide contains 1 molecule of nitrogen, or 2 atoms of nitrogen, for nitrogen molecules are diatomic (deduction from Avogadro's hypothesis). Thus the formula for nitrous oxide is N_2O_x, where x is an integer. Now, the density of nitrous oxide, as determined experimentally, is 22. Therefore, the molecular weight of nitrous oxide is 44. Of these 44 parts, 28 parts are accounted for by two atoms of nitrogen, and therefore 16 parts are to be accounted for by oxygen. But 16 is the atomic weight of oxygen. Therefore $x = 1$, and the molecular formula for nitrous oxide is N_2O.

Q. 3. *How is dry sulphur dioxide prepared? Give a neat sketch of the apparatus used. Describe experiments to demonstrate its properties.*

Explain what happens when sulphur dioxide is passed through (*a*) *bromine water*, (*b*) *solution of caustic soda*, (*c*) *concentrated nitric acid. Give equations.*

Ans. In the laboratory sulphur dioxide is prepared by heating copper turnings with concentrated sulphuric acid. Some copper turnings are taken in a flask fitted with a thistle funnel and a delivery tube. Concentrated sulphuric acid is poured down the thistle funnel till the end of the funnel remains dipped under the surface of the acid.

The flask is then placed on a piece of wire-gauze and heated with a Bunsen burner till the gas begins to be evolved. The source of heat is then removed and the gas is collected by the upward displacement of air. The gas is fairly dry and pure, but may be further dried by passing through a wash bottle containing concentrated H_2SO_4 and collected over mercury.

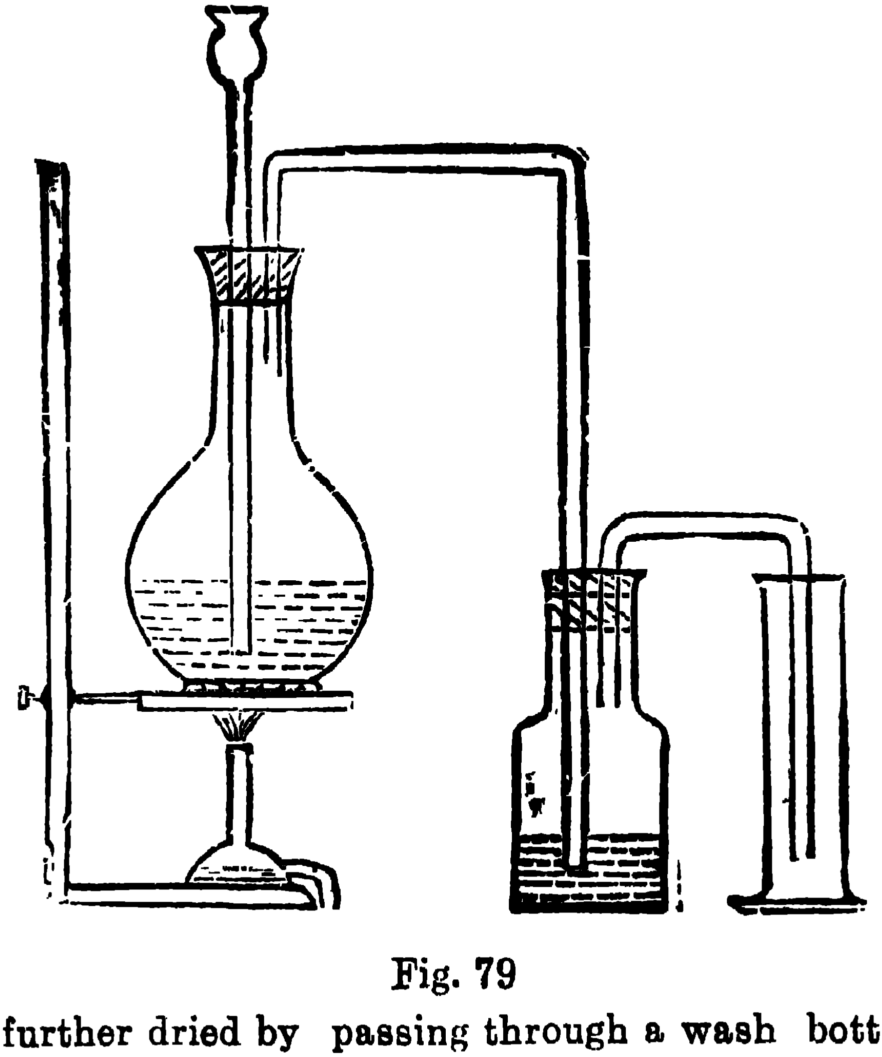


Fig. 79

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Experiments demonstrating the properties of sulphur dioxide :

(*a*) A lighted candle is plunged into a jar containing sulphur dioxide gas. The gas does not burn and the candle is extinguished. This experiment proves that SO_2 is neither combustible nor a supporter of combustion.

(*b*) A flask is fitted with a cork through which a glass tube with a drawn out end is passed inside the flask nearly to its bottom. The flask is filled with SO_2 by displacement of air and the cork with the glass tube is replaced. The flask is then inverted and the end of the glass tube, remaining outside, fitted with a piece of rubber tubing closed with a pinch cock, is dipped into blue litmus solution. The flask is then cooled and the pinchcock opened, when blue water slowly rises through the glass tube and as soon as a single drop reaches the top of the glass tube, water rushes up and enters the flask in the form of a fountain. The colour of litmus solution inside the flask becomes red.

This experiment shows that SO_2 readily dissolves in water and the solution is acidic to litmus.

(*c*) (*i*) SO_2 is passed into a pink solution of potassium permanganate containing a little H_2SO_4. The solution turns colourless, through the formation of manganous sulphate in solution.

(*ii*) SO_2 is passed through a yellow solution of ferric chloride. The solution becomes colourless due to the formation of ferrous chloride.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

These two experiments show that SO_2 possesses reducing properties. This property is also proved by passing SO_2 though Br_2-water when the yellow solution of bromine turns colourless due to formation of hydrobromic acid by reduction,

$$SO_2 + Br_2 + 2H_2O = 2HBr + H_2SO_4.$$

(*d*) Red flowers, moistened with water are introduced into a jar of SO_2 ; the flowers are bleached.

This experiment proves that SO_2 possesses bleaching properties, the moist vegetable colour being bleached by it.

(*e*) SO_2-gas is passed into a red solution of magenta. The red magenta solution is turned colourless. This also shows the bleaching property of SO_2.

(*f*) Pass SO_2 gas through H_2S dissolved in water. Sulphur is precipitated. This experiment proves that SO_2 can behave sometimes as an oxidising agent. $2H_2S + SO_2 = 2H_2O + 3S$.

(*a*) When sulphur dioxide is passed through bromine water the yellow colour of the solution is discharged. Bromine is reduced by sulphur dioxide in presence of water to hydrobromic acid and so the solution turns colourless. Sulphur dioxide is oxidised to sulphuric acid.

$$Br_2 + SO_2 + 2H_2O = 2HBr + H_2SO_4.$$

(*b*) When sulphur dioxide is passed through a solution of caustic soda, at first sodium sulphite is formed, but on passing more sulphur dioxide in presence of water, sodium sulphite is changed into sodium bisulphite which remains in solution.

$$2NaOH + SO_2 = Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3.$$

(*c*) When sulphur dioxide is passed through concentrated nitric acid, sulphur dioxide is oxidised to sulphuric acid and nitric acid is reduced to nitrogen peroxide which is evolved as a brown vapour.

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.$$

Q. 3. *Alternative. How is hydrobromic acid gas prepared in the laboratory? Give a neat sketch of the apparatus used. Describe the properties of the gas.*

Explain what happens when an aqueous solution of hydrobromic acid is treated with (a) chlorine, (b) sodium carbonate, (c) metallic zinc. Give equations.

Ans. Hydrobromic acid is prepared in the laboratory by the action of bromine on a mixture of red phosphorus and water.

In a flask fitted with a dropping funnel and a delivery tube, a mixture of red phosphorus and water is taken. The end of the delivery tube is connected with a U-tube containing glass beads with moist red phosphorus to absorb any bromine vapour that may escape from the flask. Then bromine is gradually added from dropping funnel. Hydrobromic acid gas is given off, mixed with Bromine vapour. As the mixture passes through the U-tube, Bromine vapour is absorbed by moist red phosphorus. Hydrobromic acid gas passes on and can be collected by the upward displacement of air. The flask is to be

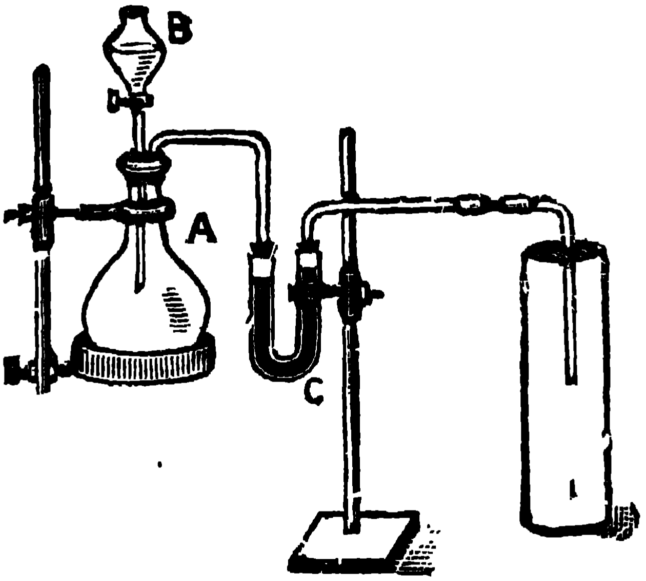


Fig. 80

gently heated towards the end of the reaction for liberating all the hydrobromic acid vapour.

If a solution of hydrobromic acid is to be prepared : the delivery tube is attached to the stem of a funnel the mouth of which is just dipped under the surface of water contained in a beaker. This arrangement prevents back suction.

$$4P + 10Br_2 = 4PBr_5 \; : \; PBr_5 + 4H_2O = 5HBr + H_3PO_4$$
$$4P + 6Br_2 = 4PBr_3 \; : \; PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

Properties of hydrobromic acid gas.—

Hydrobromic acid gas is colourless, possesses pungent smell, fumes in moist air and is highly soluble in water. It is neither combustible nor a supporter of combustion. It is readily attacked by chlorine, bromine being liberated and HCl formed by combination of chlorine with hydrogen. $2HBr + Cl_2 = 2HCl + Br_2$. It is acidic in character, as the name signifies, turns moist blue limus paper red and forms salts when passed into solutions of bases or into basic oxides suspended in water.

$$NaOH + HBr = NaBr + H_2O$$
$$CuO + 2HBr = CuBr_2 + H_2O.$$

✓(*a*) When a solution of hydrobromic acid is treated with chlorine, bromine is liberated and the solution turns yellow. Hydrochloric acid is also formed in solution.

$$2HBr + Cl_2 = 2HCl + Br_2.$$

(*b*) When a solution of hydrobromic acid is treated with sodium carbonate, sodium bromide is formed in solution, carbon dioxide gas is evolved and water is produced which forms part of the solution.

$$Na_2CO_3 + 2HBr = 2NaBr + CO_2 + H_2O.$$

(*c*) When a solution of hydrobromic acid is treated with metallic zinc, zinc bromide is formed in solution and hydrogen is evolved as gas.

$$Zn + 2HBr = ZnBr_2 + H_2.$$

Q. 4. *Describe the ammonia-soda process for the manufacture of sodium carbonate. How would you obtain caustic soda from it ? State the uses of these substances.*

Explain, giving equations, what happens when a solution of caustic soda is added to a solution of (*a*) *zinc sulphate,* (*b*) *ferric chloride,* (*c*) *mercurous nitrate.*

Ans. In the ammonia-soda process for the manufacture of sodium carbonate, a strong solution of sodium chloride (brine), directly pumped from a salt-bed after pumping in water there, is first saturated with ammonia and the ammoniated brine is next treated with carbon dioxide gas. The following reactions take place and sodium bicarbonate is deposited in the solid state :—

$$NaCl + NH_3 + H_2O + CO_2 = NH_4Cl + NaHCO_3.$$

The solid sodium bicarbonate is collected and then heated, when sodium carbonate is obtained.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The working of the process is as follows :—

(*a*) A strong solution of sodium chloride, obtained as stated above; is first collected into a brine tank (shown on the left top of the diagram). Brine from that reservoir is next admitted into the saturating tank, which is an upright cylinder. Here the brine is saturated with ammonia. The salts of calcium and

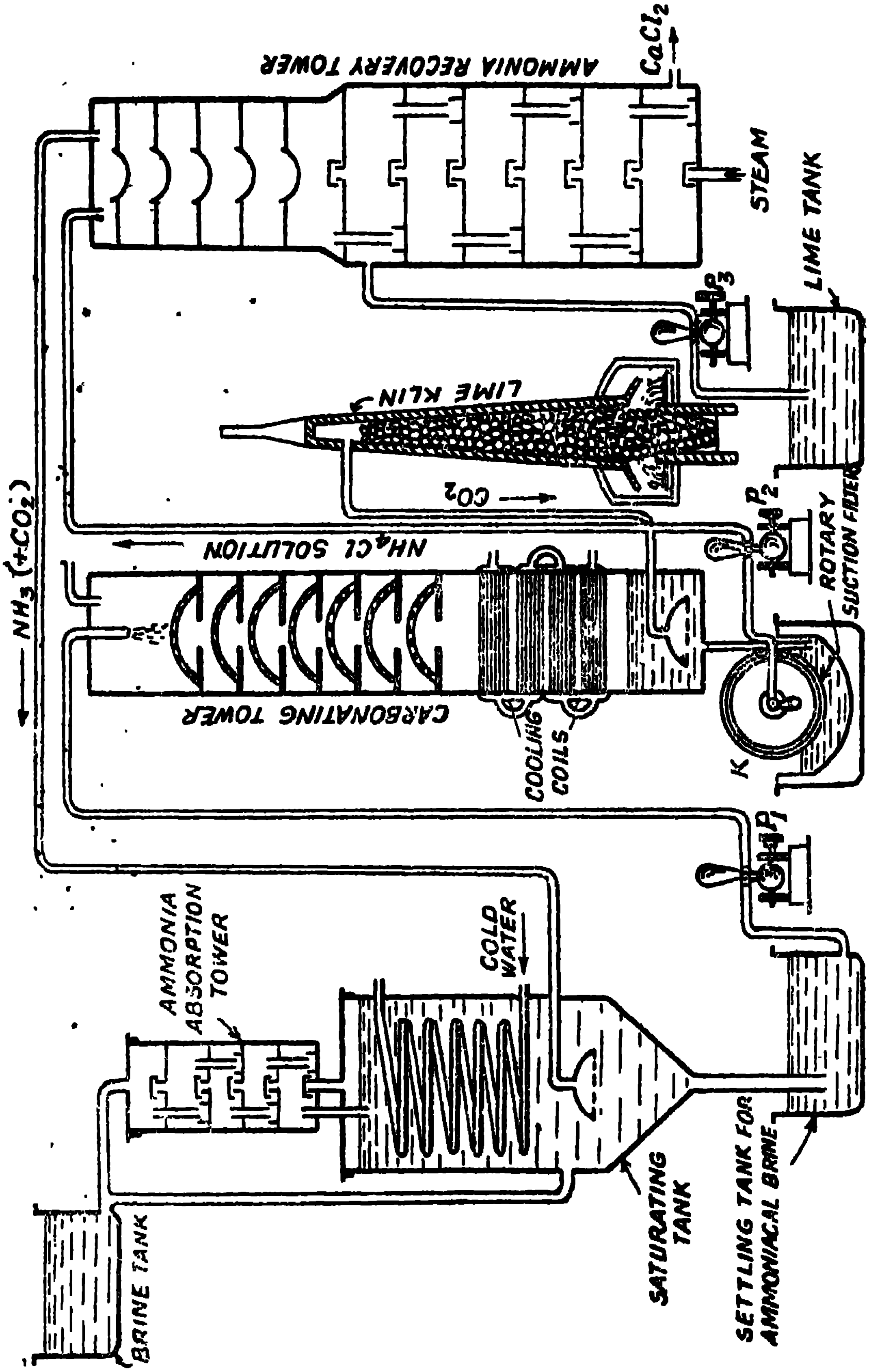


Fig. 81

magnesium, contained in the brine are precipitated by carbon dioxide, coming along with ammonia from the ammonia recovery plant :—

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$
$$CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + CaCO_3$$
$$MgCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + MgCO_3.$$

The brine, when fully saturated with ammonia, is run into a settling tank, where the precipitated calcium and magnesium carbonates settle down.

(b) Ammoniacal brine is then pumped up from the settling tank to the top of the carbonating tower, provided with perforated horizontal partitions and cooling coils and is made to trickle down the tower. Carbon dioxide gas is admitted at the bottom of the tower, so that carbonation is carried out on the principle of counter currents. Carbon dioxide rises in small bubbles through the perforations. The ammonium bicarbonate formed by the interaction of carbon dioxide, ammonia and water, reacts with sodium chloride solution, precipitating sodium bicarbonate :

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$
$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

The milky liquid containing small crystals of sodium bicarbonate is drawn off at the base of the tower and filtered at the rotary vacuum filter. The crystals of sodium bi-carbonate are deposited as a layer on the outside of the filter and are collected by scraping with a knife-blade. The mother-liquor containing ammonium chloride and some ammonium bicarbonate is pumped to the top of ammonia recovery tower.

The sodium bicarbonate is next calcined in a covered pan on a rotary furnace fired on the outside. Sodium carbonate is formed and carbon dioxide and steam escape as gas :

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide evolved here is utilised in the carbonating tower together with the gas from the lime-kiln.

(*c*) In lime-kiln limestone is heated strongly to give carbon dioxide and calcium oxide (quicklime) :—

$$CaCO_3 = CaO + CO_2.$$

The carbon dioxide is led to the carbonating tower, while the quicklime is slaked with a large quantity of water and pumped on to the ammonia-recovery plant in the form of milk of lime.

(*d*) In the ammonia-recovery tower, which consists of an upper and a lower part, the mother liquor is fed into the top of the upper part and at the top of the lower part, milk of lime is admitted. A current of steam is next admitted at the base of the tower. Ammonium bicarbonate is decomposed by steam, and ammonium chloride is decomposed by lime :—

$$NH_4HCO_3 = NH_3 + H_2O + CO_2$$
$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

The mixture of ammonia with the small amount of carbon dioxide passes on to the saturating tank.

Thus the process is self-sufficient, but certain amount (about 2%) of ammonia is lost during working, and is to be replaced.

Caustic soda is obtained from sodium carbonate by the following operations :—

An aqueous solution of sodium carbonate is prepared and is run into *causticisers*, i.e., iron tanks provided with mechanical agitators and fitted with a pipe for admission of steam. Quicklime placed in an iron cage is kept dipping into the top of the solution, the stirrer is worked and steam is passed in. Sodium carbonate then reacts with calcium hydroxide formed and is practically completely converted into caustic soda.

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + \underset{\text{pptd.}}{CaCO_3}.$$

The precipitated calcium carbonate is filtered off and caustic soda solution so obtained is evaporated in iron pans to get solid caustic soda.

Uses of sodium carbonate :—

Sodium carbonate is used chiefly (*i*) as a detergent, (*ii*) in the manufacture of soap and glass, (*iii*) for removing permanent hardness in water, (*iv*) in the manufacture of caustic soda, (*v*) for the manufacture of ærated water and (*vi*) as a reagent in the laboratory.

Uses of caustic soda :—

Caustic soda is used (*i*) in the manufacture of (*a*) hard soap, (*b*) paper, (*c*) artificial silk. It is also employed for bleaching and refining oil, in purifying bauxite and in the laboratory as a reagent.

(a) When a solution of caustic soda is added to a solution of zinc sulphate, at first a white precipitate of zinc hydroxide appears, but on addition of excess of caustic soda solution the zinc hydroxide precipitate dissolves, forming sodium zincate. Sodium sulphate is also formed in solution.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4,$$

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

(b) When a solution of caustic soda is added to a solution of ferric chloride, a brown precipitate of ferric hydroxide is formed and sodium chloride passes into solution.

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

(c) When a solution of caustic soda is added to a solution of mercurous nitrate, a dark grey precipitate of mercurous oxide is formed and sodium nitrate passes into solution. Water is also formed which forms a part of the solvent.

$$Hg_2(NO_3)_2 + 2NaOH = Hg_2O + 2NaNO_3 + H_2O.$$

Q. 4. *Alternative. How are the following substances prepared and what are their uses ? :—*

(*a*) *Metallic magnesium,* (*b*) *yellow phosphorus,* (*c*) *potassium chlorate,* (*d*) *bleaching powder ?*

Ans. (*a*) Metallic magnesium is now-a-days obtained by heating magnesium oxide (MgO) with low-ash carbon at about 2000° – 2200°C. in a closed electric furance when magnesium vapour mixed with carbon monoxide is evolved. Next a large volume of hydrogen is injected into the mixture before it leaves the furnace in order to prevent reconversion of magnesium into its oxide by the reversible reaction between carbon monoxide and Mg. Vapours of magnesium are then condensed. The metal so obtained is then heated in a second electric furnace operated under high vacuum at a temperature of 900°C. when magnesium vapourises. It is condensed and collected in suitable condensers and melted and cast into ingots.

$$MgO + C = Mg + CO.$$

Uses of magnesium :—

Magnesium flash light is used for signalling and also in photography. Magnesium powder is used in pyrotechny. It is also employed in the preparation of some light alloys like *magnalium* (an alloy of magnesium and aluminium).

(*b*). Yellow phosphorus—Calcium phosphate, either of mineral origin or from boneash, is mixed with sand and coke. The mixture is then fed into an electric furnace by means of a hopper and an Archimedian Screw arrangement.

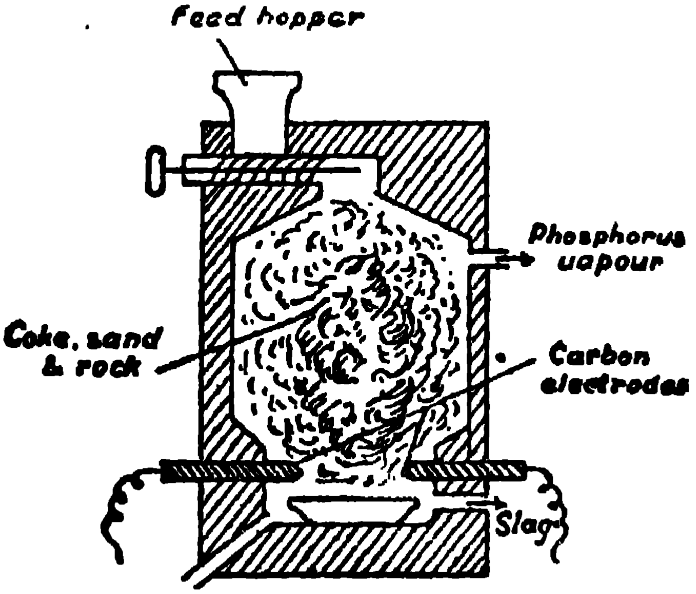


Fig. 82

The electric furnace is made of brick-work and is provided with an outlet above for the gases and phosphorus vapour, a slag-hole at the bottom and carbon electrodes, set a little above the bottom level as shown in the figure, between which an electric arc is struck, producing a high temperature.

At the temperature of the electric arc, silica reacts with calcium phosphate, producing calcium silicate and phosphorus pentoxide, P_2O_5 :—

$$Ca_3(PO_4)_2 + 3\ SiO_2 = 3CaSiO_3 + P_2O_5$$

The vapour of P_2O_5 so formed is then reduced by carbon and carbon monoxide is formed and phosphorus is set free in the form of vapour.

$$2P_2O_5 + 10C = 4P + 10CO.$$

Calcium silicate is obtained in molten condition and sinks to the bottom, from whence it is removed by opening the slag-hole. Phosphorus vapour and carbon monoxide escape through the outlet near the top and are passed into water contained in a covered tank provided with an exit pipe. Here phosphorus vapour condenses as yellow phosphorus and CO escapes as gas from the exit pipe. Fresh mixture is introduced from time to time and the process is continuous.

Uses :—Yellow phosphorus is used in preparing red P, phosphorus bronze, as a rat-poison and in incendiary bombs.

(*c*) *Potassium chlorate.*—Potassium chlorate is now-a-days prepared on an industrial scale by the electrolysis of an aqueous solution of potassium chloride KCl, at 80°—90°C., the cathode and anode being kept in the same compartment.

The apparatus consists of lead-lined wooden vessel providedl with mechanical stirrers, in which a conc. solution of KCl containing a little amount of HCl is taken. The anode is made o' platinum-iridium, and the cathode is of iron. A little potassium chromate is added to the solution in order to prevent cathodic reduction of potassium chlorate formed. Electric current is passed, when first of all potassium is liberated at the cathode, but this potassium at once reacts with water present there, producing KOH and evolving hydrogen as gas. Chlorine is liberated at the anode. The temperature of the solution rises spontaneously and is adjusted at about 80°—90°C. At the temperature mentioned chlorine reacts with potassium hydroxide solution, which is hot and concentrated, with the production of potassium chlorate and potassium chloride. The solution is taken out, concentrated and cooled when $KClO_3$ crystallises out, leaving KCl in solution, the chlorate being less soluble than chloride. The solution is used over again.

$$KCl \rightarrow K' + Cl'$$

$$\left.\begin{aligned} K' + e &= K \\ 2K + 2H_2O &= 2KOH + H_2 \end{aligned}\right\} \text{at the cathode.}$$

$$Cl' = Cl + e$$

$$Cl + Cl = Cl_2 \text{ (at the anode),}$$

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Uses :—Potassium chlorate is used in the preparation of oxygen in the laboratory, in the manufacture of matches ; in explosives ; in fireworks ; as an oxidising agent and in medicine.

(*d*) .*Bleaching powder* :—In modern works, bleaching powder is manufactured with the help of large rotating inclined iron cylinders which are cooled externally by water spray. Dry slaked lime, containing only 4% water, is fed in at the top and electrolytic chlorine diluted with air is fed in at the bottom. The reaction is vigorous. The temperature is kept below 40°C. The bleaching powder formed is discharged at the bottom and packed in barrels.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Uses :—Bleaching powder is used as an oxidising, bleaching and chlorinating agent, as a germicide and for water purification.

Q. 5. *Name the important ores of iron and give their formulas. Describe how cast iron is produced in the blast furnace. What is the difference between cast iron, steel and wrought iron? State their respective uses.*

Iron is known to form two types of salts. Give examples with formula. Describe experiments by which they may be distinguished.

Ans. Important ores of iron are

(1) Magnetite, Fe_3O_4

(2) Red Hœmatite, Fe_2O_3.

(3) Brown Hœmatite or Limonite, $2Fe_2O_3$, $3H_2O$.

(4) Spathic iron ore, Spathose or Siderite, $FeCO_3$. Iron pyrites, FeS_2, though found abundantly and possessing a large amount of iron, is never used as an ore of iron on account of its high sulphur content.

The ores generally employed for the extraction of iron are the oxides and the carbonate. Preliminary concentration of the ore is found very often unnecessary, because the naturally occurring ore is sufficiently rich in iron to be used directly in the operation. The ores mentioned are first roasted in order to drive off water and carbon dioxide, to render the mass porous and to convert ferrous oxide formed (in case of spathic iron ore) to ferric oxide. The oxide, thus obtained, is then mixed with limestone and coke and heated in a blast furnace which is made of steel and lined inside with fire-bricks. It is from 50 to 80 ft. in height usually, but in modern American practice, is made even 120 ft. high. It is broadest at the middle and is tapering towards the bottom. The broadest part, known as the *bosch*, is supported on wrought-iron pillars. The top of the furnace is closed by a *cup-and-cone* arrangement. There is an exit-pipe set beneath the cup-and-cone arrangement to let out the gases formed inside the furnace. The tapering base, known as the hearth is pierced at two points, the holes being kept closed with clay. One that is placed above the other near the bottom is known as the slag-notch, while the other is meant for taking out molten iron produced and collected at the bottom. There are also openings in the hearth, round the base, fitted with pipes, known as tuyeres, through which hot air is blown into the furnace.

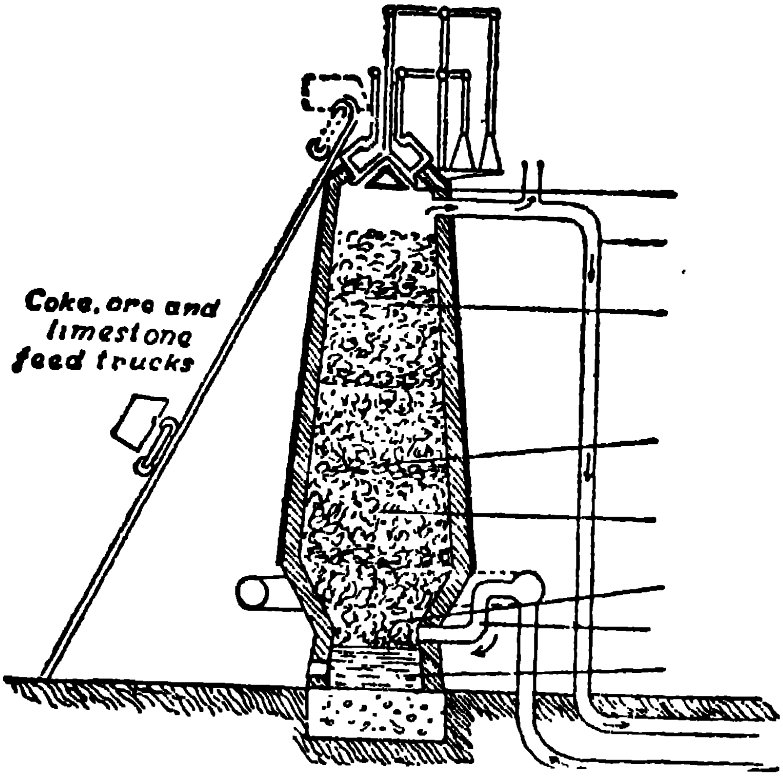


Fig. 83

The calcined ore mixed with coke and limestone is introduced into the furnace, when the furnace is lighted with faggots and is in operation, by lowering the cone. A blast of air, heated to a temperature of 700° – 800°C. with the help of Cowper's stoves, is then introduced through the tuyeres. The oxygen of the air combines with the carbon to form carbon monoxide which brings about the reduction of the iron oxide to iron.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

A portion of Fe_2O_3 which may escape reduction by CO is reduced by carbon itself. The spongy iron, so obtained at a temperature of 1000°C, absorbs various impurities like carbon, sulphur, phosphorus and silicon from the ore, coke, etc. This impure iron melts and descends to the bottom of the furnace. Lime obtained by the decomposition of the limestone at the temperature of the furnace, combines with the siliceous impurities of the ore forming a molten slag which flows down with the molten iron to the hearth. The slag, being lighter than the molten iron, floats on its surface, and thus prevents oxidation of the iron by the oxidising action of the blast.

$$CaCO_3 = CaO + CO_2$$

$$CaO + SiO_2 = CaSiO_3. \text{ (Slag)}.$$

As the slag reaches a certain height, it is made to run out through the slag-notch by piercing it with iron rods. The iron is also run out at intervals and allowed to flow into sand-moulds. Iron, thus obtained, is known as pig iron or cast iron.

The gas-mixture, consisting of 2 volumes of carbon monoxide and 1 volume of carbon dioxide, passes out by the exit-pipe at the top to a dust-catcher where dusts are deposited. The gas-mixture is then burnt in Cowper's stoves which are utilised for preheating the air-blast introduced into the blast furnace.

The essential difference to be mentioned, existing between the three forms of iron, is in their carbon content, steel being intermediate in composition to wrought iron and cast iron. Cast iron is the impurest form of commercial iron, containing 2 to 5% of C, and also S,P,Si, Mn, etc. as impurities. Wrought iron is the purest form of commercial iron, containing 0·12 to 0·25%C, and other impurities only in traces. Steel contains 0·25 to 1·5%C., and traces of other impurities. Sometimes various elements, both metallic and non-metallic, are added to steel in order to improve its qualities for various uses to which it is put.

The essential points of difference in properties with their respective uses are mentioned in the following table :

Properties	*Cast iron*	*Steel*	*Wrought iron*
1. Melting point	1200°C.	1300° – 1400°C.	1500°C.
2. Brittleness or Malleability	Brittle	Malleable and brittte	Malleable
3. Hardness	Hard	Hard and soft	Soft
4. Structure	Crystalline	Crystalline	Fibrous
5. Tempering	Cannot be tempered	Can be tempered	Cannot be tempered.
6. Welding	Cannot be welded	Can be welded	Cannot be welded
7. Magnetisation	Cannot be permanently magnetised	Can be permanently magnetised.	Cannot be permanently magnetised.
Uses	Cast iron is used for making cast articles like cooking vessels, railings, ornamental articles etc. It is also employed in the manufacture of wrought iron and steel.	Steel is used in the manufacture of (1) iron rails for railway lines, locomotives, joists, cranes, etc. (2) implements of war like cannon, swords, armoured cars etc., (3) cultery, for manufacture of knives, rajors, surgical instruments etc. ; (4) artificial magnets, watch-springs etc.	Wrought iron is employed in the preparation of electro-magnets, piano-wire and wire-netting.. All iron articles of commerce produced by hammering is obtained from wrought iron.

Iron forms two types of compounds, ferrous and ferric, differing in the valency state of iron in the two sets. Thus, we have salts like ferrous chloride, $FeCl_2$, $4H_2O$, ferrous sulphate,

$FeSO_4, 7H_2O$, ferrous carbonate, $FeCO_3$. Also we know ferric sulphate $Fe_2(SO_4)_3$, ferric nitrate, $Fe(NO_3)_3$, $6H_2O$.

Experiments for distinguishing ferrous and ferric compounds :—

1. (*a*) To a solution of a ferrous salt, potassium ferrocyanide solution is added. A white precipitate is formed in complete absence of air.

(*b*) To a solution of a ferric salt, potassium ferro-cyanide solution is added, when a dark blue precipitate is obtained.

2. (*a*) To a solution of a ferrous salt, potassium ferri-cyanide solution is added. A dark blue precipitate is obtained.

(*b*) To a solution of a ferric salt, potassium ferri-cyanide solution is added. No precipitate is formed, but a brown or green coloration is produced.

3. (*a*) To a solution of a ferrous salt, caustic soda solution is added. A green precipitate is usually obtained. In complete absence of air the precipitate is white in colour.

(*b*) To a ferric salt solution, caustic soda solution is added. A brown precipitate is obtained.

4. (*a*) Ammonium thiocyanate solution, is added to a ferrous salt solution, completely free from any ferric compound. No coloration is produced.

(*b*) Ammonium thiocyanate solution is added to a ferric salt solution. The colour of the solution becomes blood-red.

SECOND PAPER

Q. 1. *Draw a sketch of the Liebig's condenser. Name a liquid and describe, giving details, the method of preparing it in the pure state in the Laboratory involving the use of a Liebig's Condenser.*

Ans. A Liebig's condenser consists of a glass tube of a small bore with a wide funnel attached at one end as shown in the figure, provided with a jacket of a wide glass tube having two small side tubes near the two ends. The jacket tube is harmetically sealed on to the inner smaller tube.

Let the liquid chosen for purification be water. Water, as naturally obtained, usually contains two kinds of impurities, suspended and dissolved. Suspended impurities are removed by filtration, then dissolved impurities are removed by distillation. But dissolved gaseous impurities cannot be removed in this way, but the first portion of the distillate being rejected up to one-third portion, the middle one-third portion of the distillate being collected in a clean vessel (called *receiver*) and the remaining one-third being rejected in the distilling flask, the middle fraction is the pure water obtained by distillation. [But this is not absolutely pure water. Absolutely pure water is obtained from the pure water obtained by distillation by chlorinating it while boiling, removing excess of chlorine, boiling after adding a strong solution of $KMnO_4$ and KOH and then distilling and condensing the water vapour with a *silver* or *tin* coil condenser. The middle portion is also here collected to get very pure water.]

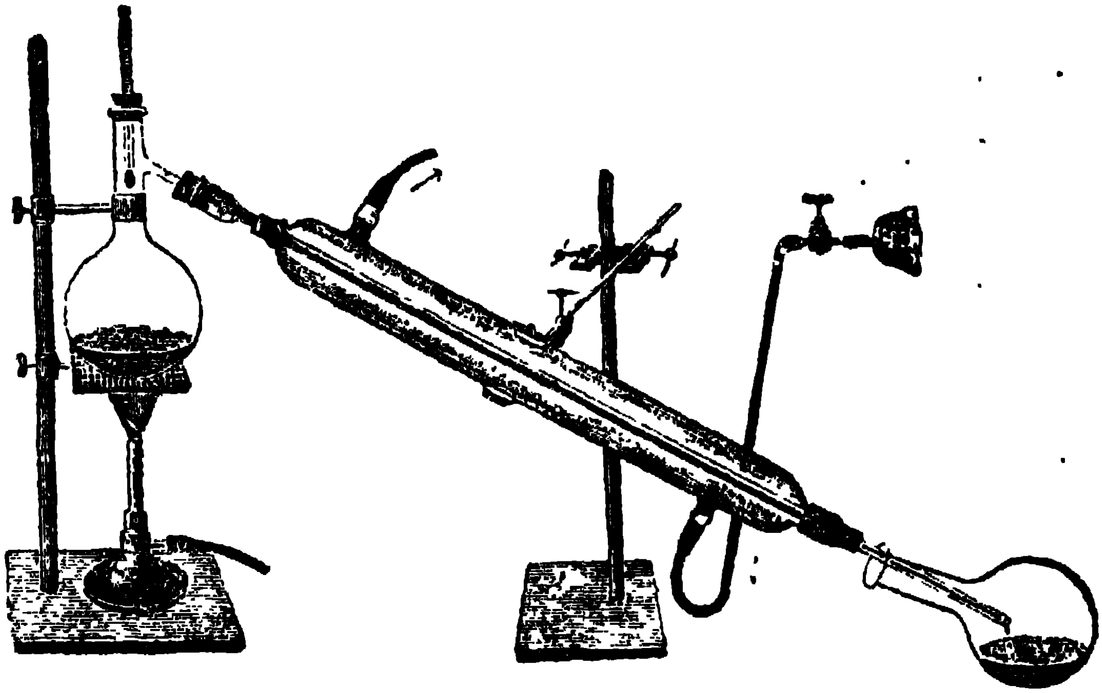


Fig. 84

The process of distillation is carried out in the apparatus arranged as shown in the figure (see Fig. 84). Filtered water is taken in the distilling flask. The side tube of the distilling flask is introduced through a cork into a Liebig's condenser as shown in the figure. Cold water enters the jacket by the lower side tube and after circulating round the narrow inner tube, and getting heated in contact with steam passing through the inner tube leaves by the upper side-tube. The arrangement for this cold water circulation through the jacket is shown in the above figure. A clean flask (called a receiver) is placed at the other end of the condenser for collecting the condensed water. A thermometer is introdued into the distilling flask through a cork fitted to its neck. The bulb of the thermometer is placed slightly below and nearly opposite to the side-tube of the distilling flask as shown in the figure. The distilling flask containing water is then heated over a piece of wire gauze, by means of a Bûnsen flame, till the liquid in the flask boils. The vapour of water, given off during boiling, passes through the inner tube of the Liebig's condenser and condenses back into liquid water there due to the cooling action of cold water circulating through the jacket and collects inside the receiver after trickling down the inner tube. The water collecting in the receiver is called the distillate. The thermometer indicates the boiling point of water, being the temperature of steam and so indicates the purity of the water vapour.

Here, if stress be laid upon *preparation* of a liquid in the pure state, we are to describe the preparation of pure bromine by similar operation on commercial bromine.

Q. 1. *Alternative. Describe a Bunsen Burner and the essential parts thereof. Explain how a candle flame is produced. Compare the structures of a Bunsen flame and a candle flame when :—*

(1) *the air hole in the Bunsen Burner is shut ; and*

(2) *the same is open.*

Ans. Bunsen Burner is the standard burner in which gas is burnt for getting heat from it in the laboratories. It consists of the following parts :—

(1) The base, generally circular, heavy and massive to keep the burner upright, having a *side-tube* which is connected by means of a rubber tube with the gas-tap for supply of gas to the burner. The side-tube communicates inside with an upright *jet* set at the middle of the base. The gas-tap being opened, the gas comes out of the *jet* (orifice), and when lighted, burns with a long, thin vertical flame.

(2) An upright tube called the burner-tube, which can be screwed round the jet. It is provided with a single or a couple of holes near its lower end. The holes are called 'air-holes'.

(3) At the base of the burner round the air-holes there is a round ring surrounding the burner-tube also carrying one or sometimes two oval holes. This part is called the collar. The air-holes in the burner-tube can be closed, partially closed, or opened by rotating this collar, which is therefore often-times called *air-regulator.*

When the burner-tube is inserted into the foot of the Bunsen burner and gas is allowed to pass, as the gas comes out of the fine orifice, a partial rarefaction is produced in the immediate neighbourhood of the jet. Thus, air is drawn in through the air-hole, and inside the burner-tube, a mixture of air and gas is obtained which comes out and burns at the top of the burner-tube. By turning the air-regulator, the proportion between gas and air going up the burner-tube can be regulated and thus a steady flame can be obtained in position upon the top of the burner-tube as shown in the figure.

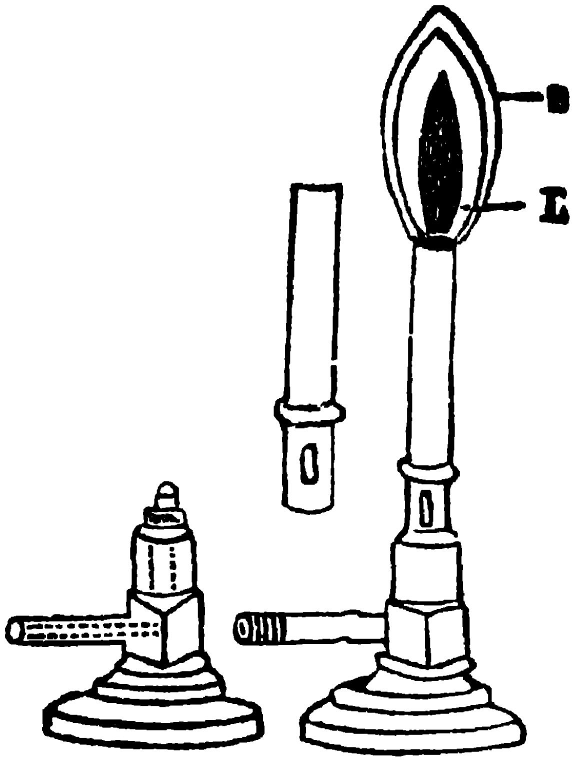


Fig. 85

The inflammable matter, of which candle is made of, is the wax or tallow consisting of compounds containing carbon and hydrogen. When a candle is lighted, the solid wax or tallow melts and is drawn up into the wick due to the capillary action and is ultimately converted into a vapour which burns in air producing a candle flame.

(1) The candle flame and a Bunsen flame when air-hole in the Bunsen burner is shut, *i.e.*, a luminous Bunsen flame, are similar in structure. The flame in both cases consists principally of three regions or zones :—

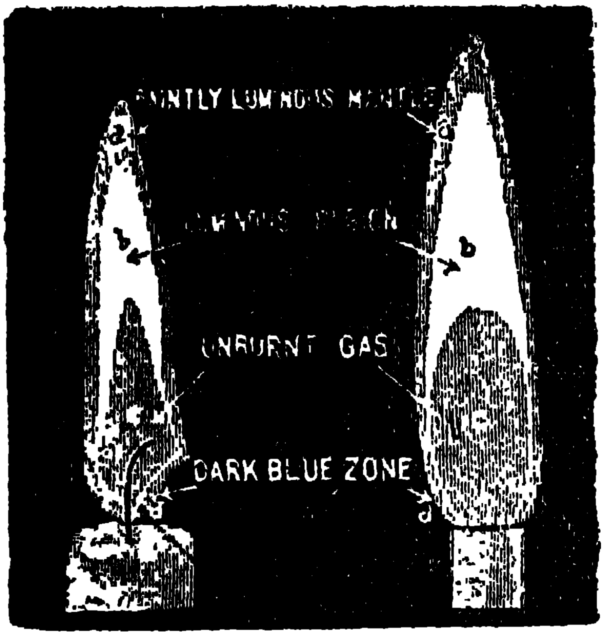


Fig. 86

(*a*) The dark central region or zone, *c* (see Fig. 86), surrounding the wick in the candle flame and just above the burner-tube in Bunsen burner, containing unburnt vapours or gases (produced from the melted wax or tallow in the case of the candle flame and hydrocarbon gases issuing out of the jet and coming up the burner-tube in the case of Bunsen flame). This is the *zone of no combustion.*

(*b*) Above this there is the bright region, *b*, which is coloured yellow in both cases. *This is the luminous middle zone of incomplete combustion.* Here solid particles of carbon are found to separate out.

(*c*) Then comes the faintly luminous outer region, *a*. It surrounds the entire flame. *This is the zone of complete combustion.*

Over and above the regions mentioned there is seen a small region, *d*, at the base of the flame which appears bright blue in colour and is non-luminous.

(2) The Bunsen flame, when the air-hole is kept sufficiently open, consists of two distinct zones or regions, (*a*) the innermost blue zone of no combustion, and (*b*) the outermost non-luminous zone of complete combustion.

Thus, the Bunsen flame in this case and the candle flame differ in the following respects :—

(*a*) Three zones are found in a candle flame whereas two zones are found in a Bunsen flame under this condition.

(*b*) The flame is luminous in a candle flame but non-luminous in a Bunsen flame of this type.

(*c*) The flame of a candle is shorter in size but that of a Bunsen burnor is longer, but the flame is shorter in size in comparison to a luminous Bunsen flame.

(*d*) A candle flame gives a lower temperature than a Bunsen flame under this condition because greater amount of combustion is going on in the latter.

But if the air-holes be opened to a greater extent, the quantity of air sucked in is greater than what is required to destroy luminosity, the colour of the inner zone becomes green and the flame begins to roar. If more air be gradually admitted, the flame '*strikes back*', that is, the gas begins to burn at the jet.

Q. 2. *1·3456 grams of Sodium Carbonate are dissolved in water and the volume of the solution is made up to 250 c.c. in a measuring flask by gradual careful addition of water. 25 c.c. of this solution are delivered into a porcelain basin by means of a pippet and exactly neutralised by 24·85 c.c. of a solution of Sulphuric acid run down into it from a burret in drops using methyl orange as an indicator. Calculate :—*

(*a*) *The normality of the Sodium Carbonate solution ;*

(*b*) *The normality of the acid solution ;*

(*c*) *The amount of Sodium Sulphate formed on neutralisation.* (Na = 23·0, C = 12·0, O = 16·0).

Ans. Since 250 c.c. of the Sodium Carbonate solution contains 1·3456 grams of Na_2CO_3 (anhydrous), therefore, 1000 c.c. of the Sodium Carbonate solution contains 1·3456 × 4 or 5·3824 grams of Na_2CO_3 (anhydrous).

Hence, the strength of Na_2CO_3 solution $= \frac{5·3824}{5·3} . \frac{N}{10}$

$$= 1·0155 . \frac{N}{10} = 0·10155\ (N)$$

Let S be the strength of Sulphuric acid solution.

Then, we have

$$25 \times 0·10155\ (N) = 24·85 \times S$$

$$\therefore\ S = \frac{25}{24·85} \times 0·10155 (N)$$

$$= 0·10216\ (N).$$

From the equation

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = \underset{142}{Na_2SO_4} + CO_2 + H_2O$$

We know that

106 grams of Na_2CO_3 give rise to 142 grams of Sodium Sulphate on being neutralised with H_2SO_4.

Therefore, 1 gram of Na_2CO_3 will give rise to $\frac{142}{106}$ gm. Na_2SO_4.

Hence, 0·13456 gm. of Na_2CO_3 which is present in 25 c.c. of the solution used will give rise to $\frac{142}{106} \times 0·13456$ gm. Na_2SO_4,

that is 0·18026 gram of Na_2SO_4.

Q. 3. *Alternative. What is equivalent weight of an element ? Starting from pure metallic sodium, state how you would proceed to make a fair (not exact) direct estimate of its equivalent weight ?*

Ans. The equivalent weight of an element is a number which expresses the parts by weight of the element which can combine with or displace from combination 1 part by weight of hydrogen (or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine).

Thus, the equivalent weight of calcium is 20, for 20 parts by weight of calcium can combine with or displace from combination 1 part by weight of hydrogen.

Determination of approximate equivalent weight of sodium :—

A little kerosine oil is placed in a weighing bottle and it is weighed in a chemical balance. A bit of sodium is taken from under kerosine oil in which it is kept and dried quickly within folds of filter paper and taken inside kerosine oil placed in the weighing bottle, taking care that no kerosine oil is lost by splashing. The weighing bottle with kerosine oil and a bit of sodium is weighed again. The difference gives the weight of sodium taken. The bit of sodium is then transferred to a hard glass tube closed with corks at two ends. Two glass tubes are fitted to the corks at two ends, one for letting in, and the other for exit of, gas. The hard glass tube with sodium is heated and chlorine gas is led in when sodium is converted into sodium chloride. The current of chlorine is continued till all the sodium is converted into its chloride. This chloride is transferred to a weighed dry weighing bottle by transferring it after cooling the hard-glass tube to room temperature with a camel hair brush to glazed paper and thence to the weighing bottle. The weighing bottle with the sodium chloride is weighed again. The difference gives the weight of sodium chloride formed.

Let W_1 gm. be the weight of sodium taken and W_2 gm. be the weight of sodium chloride formed. Therefore $(W_2 - W_1)$ gram of chlorine has combined with W_1 gm. of sodium.

Therefore, the equivalent weight of sodium, by definition

$$= \frac{W_1}{W_2 - W_1} \times 35{\cdot}5.$$

Q. 3. *Describe the method of preparation in the Laboratory as well as the manufacture in the industries with a brief reference to its storage of some gas with which you are familiar. What test is applied to identify the gas ?*

Ans. Chlorine is the gas taken for discussion.

(*a*) Chlorine is prepared in the laboratory by heating concentrated hydrochloric acid with manganese dioxide. Small lumps of manganese dioxide (naturally occurring pyrolusite) are taken in a flask provided with a thistle funnel and a delivery tube passing through the cork fitted to the mouth of the flask. Conc. HCl is poured down the thistle funnel so that it covers MnO_2 and the end of the thistle funnel dips into the acid. A deep brown solution is produced in the flask. The flask is clamped to a stand above a piece of wire-gauze and is connected by the delivery tube with a flask containing water for washing HCl vapour also evolved during heating. The end of the tube dips under water and another tube fitted to the cork attached to the mouth of the second flask so that it starts just from the top and is bent twice at right angles, serves as the delivery tube. The flask is gently heated with a Bunsen burner. Chlorine is evolved and is passed through water in the second flask to free it from HCl vapour and is then collected by the upward displacement of air.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

(*b*) Chlorine is now-a-days manufactured by electrolysis of brine in a diaphragm cell. The anodes are carbon rods fitted to the outer compartments and the cathode is a bunch of iron rods suspended in the middle compartment. Chlorine is evolved at the carbon anodes in the two outer compartments by passing electric current through the electrodes. This is dried by passing through conc. H_2SO_4, liquefied and the liquid is stored in iron cylinders and as such it is sent out to the market.

Tests applied for identifying the gas.

The greenish-yellow colour, peculiar smell like that of bleaching powder together with its bleaching properties help to identify the gas. Moreover, by using starch-iodide paper, the gas can be further confirmed by the blueing of the paper.

Q. 4. *Alternative. Concentrated sulphuric acid when gently heated with charcoal powder evolves a gaseous mixture consisting of carbon dioxide and sulphur dioxide. How would you conclusively prove that these gases are really present and further that they are present in equal volumes.*

Ans. The reaction mentioned is represented by the equation

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.$$

Thus, from the equation, it is evident that under the same conditions of temperature and pressure, the volume of carbon dioxide : the volume of sulphur dioxide = 1 : 2. Thus in the last part of the question, equal (?) volumes is a genuine mistake.

That the gaseous mixture obtained in the above reaction is a mixture of CO_2 and SO_2 can be proved in two ways :—

(*a*) The gas mixture is passed slowly through a U-tube immersed in a freezing mixture when sulphur dioxide condenses to the liquid state and carbon dioxide gas passes on. That the escaping gas contains CO_2 can be shown by the passage of the gas through lime water which turns milky but on continuedly passing the gas the milkiness disappears and a clear solution is obtained.

$$Ca(OH)_2 + CO_2 = \underset{\substack{\text{Precipitated}\\\text{causing milkiness.}}}{CaCO_3} + H_2O$$

$$CaCO_3 + H_2O + CO_2 = \underset{\substack{\text{Soluble bicarbonate}\\\text{of calcium.}}}{CaH_2(CO_3)_2}$$

Further the escaping gas does not contain any smell of SO_2 (burning sulphur), when the latter is fully condensed by efficient cooling.

On taking out the U-tube and heating it to room temperature, SO_2 gas is evolved recognised by its smell. The gas is passed through Br_2 – water when the Br_2 – water is decolorised. Then $BaCl_2$ solution is added when a heavy white precipitate, insoluble in HCl, is obtained. The precipitate is, therefore, of barium sulphate. The reactions are

$$Br_2 + SO_2 + 2H_2O = 2HBr + H_2SO_4$$

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

(b) The gas mixture is passed through aqueous ~~acidified~~ solution of potassium permanganate when SO_2 is removed, according to the reaction.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Then, the usual test for carbon dioxide can be applied. The smell of burning sulphur present in the gas mixture together with its capacity to decolorise potassium permanganate solution is sufficient test to show the presence of sulphur dioxide in the gas mixture.

For showing the volume relationship, a certain volume of the gas mixture is passed through a known volume of standardised potassium permanganate solution (taken in excess) at first and then through a known volume of standardised baryta solution (also taken in excess). The permanganate solution is then boiled to expel any dissolved CO_2 and the gas evolved is absorbed after cooling in the baryta solution used to absorb CO_2 originally. The excess of permanganate left over as also the excess of baryta remaining are determined by titration with standard oxalic acid. From the volume of permanganate as also of baryta used up, both of known strength, we can calculate the volume of sulphur dioxide and of carbon dioxide respectively in a given volume of the gas mixture used. Thus, it is proved that the volume of sulphur dioxide : volume of carbon dioxide in the gas mixture is as 2 : 1.

The same result can be obtained by taking the mixture of gases in a Hempel's gas-burette over mercury, and after adjusting the mercury level, the volume of the mixture noted. The arm of the gas burette containing the gas mixture is cooled by jacketing it and placing freezing mixture in that jacket when SO_2 condenses to the liquid state leaving CO_2 free. The mercury level is again adjusted and the volume of CO_2 is read off. The difference gives the volume of SO_2 present in the mixture. Vol. of CO_2.: Vol. of SO_2 will be found to be 1 : 2 as before.

Q. 4. *How are pure Cuprous Chloride and pure Cuprous Iodide prepared in the Laboratory? How are they kept? What are ammoniacal and acid solutions of cuprous chloride? To what uses are they put in the Laboratory?*

Ans. Pure cuprous chloride is prepared in the laboratory by dissolving black cupric oxide, CuO, in excess of concentrated HCl in a flask. The solution so obtained is then boiled with copper turnings. When the reaction is over, the liquid is poured into a large volume of water contained in a litre beaker. A white precipitate of cuprous chloride is obtained. It is filtered, washed thoroughly with cold water and then dried.

$$CuO + 2HCl = CuCl_2 + H_2O$$
$$CuCl_2 + Cu = 2CuCl.$$

Cuprous Iodide, CuI (*not included in I.A. and I.Sc. syllabus*).

Blue vitriol, $CuSO_4, 5H_2O$ and green vitriol, $FeSO_4, 7H_2O$ are dissolved in right proportion in water and KI solution is added. White precipitate of cuprous iodide is obtained.

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_3 + K_2SO_4.$$

The solution is filtered, washed with water completely and dried over conc. H_2SO_4 in a desiccator.

When completely dry, both cuprous chloride and cuprous iodide can be kept in a well-stoppered bottle sealed with wax so that no air can enter and bring about oxidation.

Cuprous chloride is soluble in ammonia and solution so produced is known as ammoniacal solution of cuprous chloride and it contains cuproammine chloride, $Cu(NH_3)Cl, H_2O$ if all traces of oxygen are excluded. Ammoniacal Cuprous Chloride readily absorbs oxygen, forming a deep blue solution of cupriammine chloride, $Cu(NH_3)_4 Cl_2, 2H_2O$.

Similarly, cuprous chloride is soluble in conc. HCl and the solution so obtained is colourless in the complete absence of oxygen. It is known as acid solution of cuprous chloride. It readily absorbs O_2 and turns green.

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O.$$

Both ammoniacal and acid solutions of cuprous chloride are used in gas analysis for removal by chemical action of carbon monoxide, or oxygen or acetylene from a gas mixture. Acid solution of cuprous chloride is used in removing CO from a mixture of CO and CO_2.

Q. 5. *Alternative. Give an account of the isolation of fluorine by Moissan detailing the difficulties which stood in the way of its isolation before his time and pointing out how these were removed by him.*

Ans. Isolation of Fluorine by Moissan :—

Moissan isolated fluorine by electrolysing a solution of potassium hydrogen fluoride, KF,HF, in anhydrous hydrofluoric acid, HF. The apparatus used by him was U-tube made of an alloy of Platinum-Iridium, provided with two side-tubes and is fitted with fluorspar stoppers. Two electrodes made also of the same Platinum-Iridium alloy and thickened at the bottom was inserted through the fluorspar stoppers. The whole apparatus was cooled by immersing in a bath of boiling methyl chloride (b. pt. $-23°C.$). The U-tube was $\frac{2}{3}$rd. full with the electrolyte, a solution of KF,HF (Fremy's salt) in anhydrous HF. On passing current through the electrolyte, Hydrogen was liberated at the cathode and Fluorine at the anode. The fluorine was led through a spiral of platinum kept immersed in boiling methyl chloride to remove any HF vapour evolved along with Fluorine by condensation. The gas was next passed through a tube of Platinum packed with NaF in order to remove the last trace of HF from Fluorine. The gas was then collected in a Platinum vessel by the upward displacement of air.

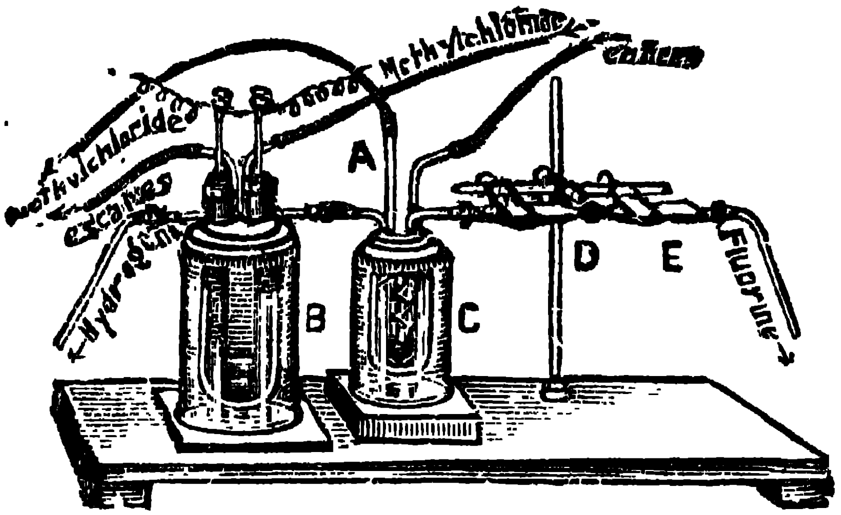


Fig. 87

The difficulties which stood in the way of isolation of fluorine were :

(1) Hydrofluoric acid cannot be oxidised by heating with MnO_2 or any other oxidising agent as in the case of other halogen acids.

(2) Anhydrous Hydrofluoric acid is a perfect non-conductor of electricity and aqueous Hydrofluoric acid on electroylsis yields hydrogen and oxygen.

(3) Suitable vessel for electrolysis could not be found, for fluorine, if evolved, attacks all the materials, Pt forming PtF_4, a chocolate powder, C forming CF_4, a gaseous compound.

(4) Also the poisonous character of anhydrous hydrofluoric acid in the vapourous state was not understood and so more than one chemist lost their lives.

Moissan in 1886 overcame these difficulties by—

(*a*) carrying out electrolytic oxidation of anhydrous HF.

(*b*) using a solution of KHF_2 in anhydrous hydrofluoric acid as the electrolyte.

(*c*) using a U-tube made of an alloy of Pt and Iridium, the electrodes being also made of the same material and the stoppers being made of fluorspar, cork or rubber being attacked by fluorine.

(*d*) preventing the evolution of HF vapour by placing the U-tube in a bath of boiling methyl chloride and any HF vapour evolved being removed by cooling with boiling methyl chloride (B. P.—23°C.), the last trace being removed by absorption in fused NaF.

Q. 6. *Give a short account of the electrometallurgy of Aluminium, detailing the following points :*

(*a*) *the ores of the metal ;*
(*b*) *the undesirable impurity in the ores ; and*
(*c*) *the method of its removal.*

Ans. (*a*) Aluminium always occurs in combination with other elements and is widely distributed. It is present to the extent of 7·3 per cent. in the earth's crust—in all **silicate rocks,** in **clay** and **slate.** Though aluminium occurs so very abundantly, yet only two of its naturally occurring compounds can be considered as its ores, viz., **bauxite,** Al_2O_3, $2H_2O$ and **cryolite,** AlF_3, 3NaF, since these two are employed in profitable and economic extraction of the metal. No method has yet been worked out for the extraction of aluminium from **clay.** The metal is exclusively extracted from bauxite.

(*b*) But bauxite contains impurities like Fe_2O_3, SiO_2, etc. The presence of these impurities in bauxite causes aluminium extracted directly from it to be contaminated with iron and silicon, thus making the metal useless, for in that case the metal is easily attacked by water.

(*c*) Hence it is necessary to purify bauxite before use in the metallurgical extraction of aluminium. This purification can be effected in either of the two ways mentioned below and pure aluminium oxide produced. Pure alumina is then used in the extraction of aluminium.

(*i*) **Hall's Process involving fusion** :—Powdered bauxite is mixed with sodium carbonate in sufficient quantity and the mixture heated to bright redness in a furnace. Sodium aluminate is formed.

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2.$$

The mass is cooled and then rapidly extracted with water. Sodium aluminate dissolves while iron oxide, etc., remain insoluble. The insoluble impurities are removed by filtration. The filtrate is heated to 50° – 60°C. and CO_2 gas is passed into the clear and hot solution of $NaAlO_2$. Aluminium hydroxide, $Al(OH)_3$, is precipitated by this treatment.

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3.$$

The precipitated $Al(OH)_3$ is separated, washed, dried and ignited, when pure Al_2O_3 is obtained.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

N. B. Sodium silicate, though present in solution, is not decomposed by carbon dioxide and so is removed in the filtrate from $Al(OH)_3$.

(*ii*) **Baeyer's Process** :—This process is applicable to red bauxite in which much Fe_2O_3 and little SiO_2 are present as impurities. Bauxite is first finely ground and then calcined below red heat. The calcined mass is digested with NaOH solution of 45% strength under 80 lb. pressure at 150°C. when Al_2O_3 goes into solution as sodium aluminate and Fe_2O_3, $Fe(OH)_3$, etc. remain insoluble. The solution is next diluted and filtered. The filtrate is next digested with a little $Al(OH)_3$ obtained from the previous operation with constant agitation, when $NaAlO_2$ is hydrolysed and nearly the whole of aluminium precipitated as $Al(OH)_3$. The precipitated $Al(OH)_3$ is collected washed, dried and ignited, when pure alumina is obtained.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$
$$NaAlO_2 + 2H_2O = 2Al(OH)_3 + NaOH.$$

(*d*) *Extraction of aluminium by the electrolysis of pure* Al_2O_3

The purified bauxite is next dissolved in fused cryolite, contained in an electric furnace made of iron in the form of a box with an inside lining of gas-carbon. The box is made the *cathode* and the *anode* consists of stout carbon rods suspended from a copper rod and kept dipped into the bath. A little fluorspar is added to the bath for increasing its fluidity and the molten bath is kept covered with a layer of charcoal. When electric current is passed in, the resistance of the electrolyte generates sufficient heat to keep the mass in the fused state (920°C.) and aluminium oxide is decomposed. Aluminium is liberated at the cathode and the liquid metal sinks to the bottom of the bath. The molten metal is taken out by means of the "tap hole". Oxygen is liberated at the anode and it attacks the carbon anodes producing CO and CO_2 in equal volumes, which are given off as gases. The process is made continuous by shunting a lamp off the circuit, so that when all the Al_2O_3 is used up, the resistance of the bath increases and thereby makes the lamp glow. Fresh alumina is then added and the process is made continuous.

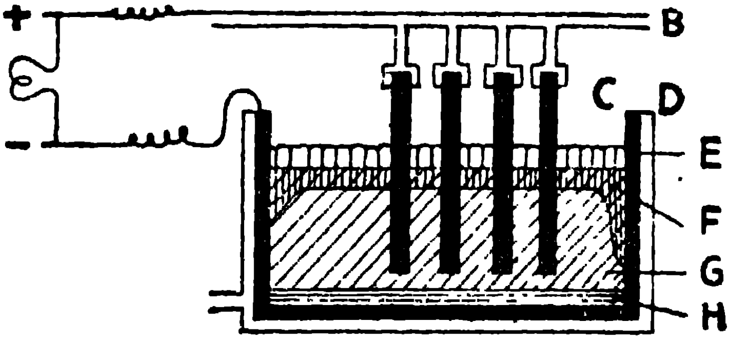


Fig. 88

$$2Al_2O_3 = 4Al + 3O_2$$
$$2C + O_2 = 2CO$$
$$C + O_2 = CO_2.$$

N. B. Cryolite, as obtained from mines in Greenland, is found to be contaminated with silica. On that account at present artificial cryolite produced in the works is used.

1952

FIRST PAPER

Q. 1. *State the laws of definite and reciprocal proportion. Show how they follow from Dalton's Atomic theory. Give examples.*

Ans. Law of definite proportion.—*The same compound always contains the same elements combined together in the same proportion by weight.*

For example, the compound *water* can be obtained from various sources, such as the sea, river, rain, spring, etc., and also it can be synthetically prepared in the laboratory. If water from any of these sources be purified and analysed, it will always be found to consist of the same two elements, hydrogen and oxygen, combined in the proportion of 1 part by weight of hydrogen to 8 parts by weight of oxygen.

Again the compound *sodium chloride* is obtained from sea-water, from dried-up lakes and also as rock-salt. It can also be obtained synthetically in the laboratory. But after purification, when any of the samples is analysed, it is found that the same two elements sodium and chlorine are present in it combined in the invariable proportion of 23 parts by weight of sodium to 35·5 parts by weight of chlorine.

Law of reciprocal proportion.—*The weights of different elements which combine separately with a constant weight of another element are either the same as, or simple multiples or sub-multiples of the weights by which those different elements combine amongst themselves.*

Otherwise stated, *if a certain weight 'x' of an element A combine with a certain weight 'y' of an element B and a certain weight 'z' of an element C, then if combination between B and C be possible, they will combine in the ratio $y : z$ or in some simple multiple of these, e.g., $y : 2z$, or $2y : z$, or $2y : 3z$, etc.*

For example, 31 grams of phosphorus combine with 3 grams of hydrogen to form PH_3 and with 106·5 grams of chlorine to form PCl_3. Hence, if hydrogen and chlorine can combine with each other, they would do so in the proportion of 3 grams of hydrogen to 106·5 grams of chlorine or in some multiple or sub-multiple of these numbers. We know that hydrogen and chlorine do combine to form HCl in the proportion of 1 : 35·5, *i.e.*, the same as 3 : 106·5.

Again, in carbon dioxide, carbon and oxygen combine in the ratio 12 : 32 and in sulphur dioxide, sulphur and oxygen combine in the ratio 32 : 32. Then, if combination between carbon and sulphur be possible, they will combine in the ratio 12 : 32 or in some multiple or sub-multiple of these numbers. Actually carbon and sulphur combine to form carbon disulphide, these two elements combining in the ratio 12 : 64, *i.e.*, as 12 : 2 × 32, 2 × 32 being a simple multiple of 32.

Dalton's Atomic theory postulates that matter is composed of discrete, very small particles called *atoms*, which cannot be further subdivided, nor can they be created or destroyed. Further, atoms of the same element are similar to one another in all respects and are equal in weight; whereas atoms of different elements possess different weights and different properties. Chemical combination between two or more elements takes place by the *juxtaposition* of the atoms of different elements in simple numerical proportions, *viz.*, as 1 : 1, 1 : 2, 1 : 3, 2 : 3 etc. The combining weights of the elements represent the combining weights of the atoms.

From the above postulates the above two laws of chemical combination can be deduced in the following way :—

Law of Definite Proportion.—When elements combine to form a compound, the combination takes place through their atoms that unite. Let us suppose that x atoms of an element A combine with y atoms of another element B to form a molecule of the compound of A and B. The weights of the elements A and B present in such a compound are in the ratio x × at. wt. of A : y × at. of B. But the atomic weights of A and B are fixed, and in the compound of A and B, these two elements are present in a fixed ratio. Thus the statement that the same compound always contains the same elements, combined together in the same proportion by weight, is found to be deducible from Dalton's Atomic Theory.

(4) *Law of Reciprocal Proportions.*—Let us suppose that

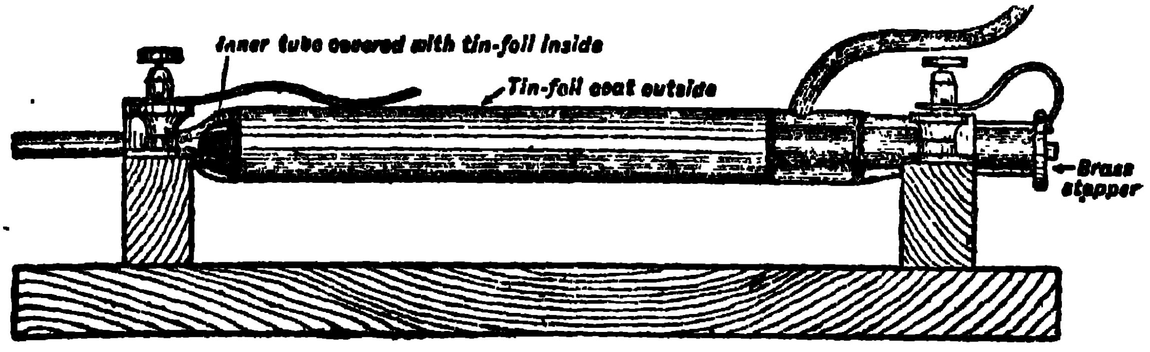
a, b and c are the at. wts. of three elements A, B and C respectively. And let one atom of A combine with one atom of B to form a molecule of the compound AB and one atom of A combine with one atom of C to form a molecule of the compound AC. Therefore, a parts by wt. of A combine with b parts by weight of B and c parts by weight of C.

(*i*) If now combination between B and C be possible, they will form a compound, either by combination of one atom of B with one atoms of C, or x atoms of B with y atoms of C, where x and y are positive integers. In the first case, the compound formed is BC and in it b parts by weight of B has combined with c parts by weight of C. Hence the weights in which B and C combine with each other are the same as the weights in which they combine separately with a fixed weight of A, *viz.*, a.

In the second case, the compound formed is B_xC_y, and in it $b \times x$ parts by weight of B is in combination with $c \times y$ parts by weight of C. Now $b \times x$ is a simple multiple of "b" and $c \times y$ is a simple multiple of "c", for x and y are positive integers. Hence the weights in which B and C combine with each other are simple multiples of the weights in which they separately combine with a fixed weight, viz., "a" of another element A.

Q. 2. *Describe the preparation, properties and uses of ozone. Give a sketch of the apparatus used for the preparation of the gas. Prove that ozone is made up of oxygen only.*

Ans. Ozone is prepared by subjecting pure and dry oxygen to silent electric discharge. The operation is carried out in Siemen's ozoniser which consists of two concentric glass tubes sealed hermetically at one end. The outer tube is coated on the



Siemens' ozoniser.

Fig. 89

outside and the inner tube on the inside with tin-foils. These tin-foils are connected in their turn to the binding screws at the base of the apparatus. These binding screws are also connected to the terminals of a Ruhmkorff's coil. Dry oxygen is passed through the annular space in slow stream and a series of silent electric discharge is passed. The gas coming out by the exit consists of a mixture of oxygen and ozone.

$$3O_2 = 2O_3.$$

The yield is only 5 to 8%.

Properties :—*Physical :* Ozone is a pale blue gas with a fishy odour. It is slightly soluble in water, but readily dissolves in certain essential oils like oil of cinnamon or oil of turpentine. It can be liquefied by passing through a tube immersed in liquid air. The liquid has a deep blue colour and boils at—112·4°C.

Chemical :—Ozone is unstable towards heat and decomposes completely into oxygen at 250° - 300°C. It is a powerful oxidising agent. It oxidises moist lead sulphide (black) to lead sulphate (white) :

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

It oxidises sulphur dioxide to sulphur trioxide and stannous chloride in HCl solution to stannic chloride ; in these two reactions no oxygen is liberated but ozone is completely used up.

$$3SO_2 + O_3 = 3SO_3$$
$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O.$$

It oxidises halogen hydracids with the liberation of the halogen elements.

$$2HCl + O_3 = Cl_2 + H_2O + O_2.$$

Moist S, P, As, etc. are oxidised to their highest oxyacids.

$$S + H_2O + 3O_3 = H_2SO_4 + 3O_2.$$

Iodine in presence of water, is oxidised by ozone to iodic acid. It liberates by oxidation iodine from neutral potassium iodide solution.

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2.$$

It attacks many metals. Mercury loses its mobility when it is brought into contact with ozone ; this is probably due to the oxidation of mercury with the production of Hg_2O which dissolves in mercury, thereby making it lose its fluidity. The mobility is restored by washing the fouled mercury with water. Silver is oxidised by ozone to silver oxide and blackening of the bright surface of silver occurs.

Ozone bleaches vegetable colours by oxidation.

An aqueous solution of ozone first reddens and then bleaches litmus. The reddening is explained by supposing the formation of ozonic acid by the action of ozone on water :

$$O_3 + H_2O = H_2O_4.$$

Ultimately the bleaching occurs due to the oxidising action of ozone.

That ozone is made up of oxygen only is proved by the fact that when pure and dry oxygen enclosed over concentrated sulphuric acid in a graduated vessel is subjected to silent electric discharge, it is converted into ozonised oxygen with contraction in volume, as indicated by the movement of the sulphuric acid level. Moreover, when ozonised oxygen is heated to 300°C., no other gas than oxygen is obtained from its decomposition.

Hence ozone is nothing but condensed oxygen.

Q. 2, *Alternative :—*

Describe the preparation and properties of nitric acid. What is the action of (i) concentrated as well as (ii) dilute nitric acid on Cu and Zn in the cold ? Give equations.

Ans. Nitric acid is prepared in the laboratory by heating gently a mixture of equal parts by weight of potassium nitrate and conc. sulphuric acid, the mixture being taken in a retort. The stem of the retort enters into a receiver which is kept cool by being floated in a trough of water and placed under a running water-tap. Nitric acid, being volatile, distils over and collects in the cooled receiver.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

*Properties :—*Nitric acid is a colourless, fuming liquid with peculiar choking smell. It has a specific gravity of 1·5 and boils at 86°C. with partial decomposition. It is highly corrosive. When it comes in contact with skin, it stains the skin yellow and produces painful wounds. It is decomposed by light and so it is preserved in amber-coloured bottles. When heated, it decomposes into nitrogen peroxide, oxygen and water.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

It is a very powerful oxidising agent. A piece of glowing charcoal burns brilliantly when thrown into concentrated nitric acid.

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O.$$

Dry and warm sawdust catches fire and burns when conc. nitric acid is poured on it. Sulphur, phosphorus and iodine are oxidised respectively into sulphuric, phosphoric and iodic acids by hot and conc. nitric acid.

$$S + 2HNO_3 = H_2SO_4 + 2NO$$
$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2$$
$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O.$$

Ferrous sulphate solution is oxidised to ferric sulphate in presence of sulphuric acid by treatment with nitric acid.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

It bleaches indigo solution. Nitric acid readily dissolves all metals except gold, platinum and iridium.

Cold conc. nitric acid dissolves copper with the formation of copper nitrate in solution and evolution of brown fumes of nitrogen peroxide.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

Cold dilute nitric acid dissolves copper with the formation of copper nitrate in solution and evolution of nitric oxide as gas.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Cold conc. nitric acid dissolves zinc with the formation of zinc nitrate in solution and evolution of brown fumes of nitrogen peroxide.

$$Zn + 4HNO_3 = Zn(NO_3)_2 + 2H_2O + 2NO_2.$$

Cold and dilute nitric acid dissolves zinc with the formation of zinc nitrate and ammonium nitrate in solution. In this case no gas is evolved,

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

Q. 3. *Deduce from Boyle's and Charles' laws the relation PV/T is a constant.*

A given mass of a gas occupies a volume of 1000 c. c. at 27°C. and 760 mm. pressure of Hg. What volume will it occupy at 327°C. and 1520 mm. pressure of Hg. ?

Ans. Boyle's law states that *temperature remaining constant the volume of a given mass of any gas varies inversely as its pressure.*

Mathematically expressed if P be the pressure and V the volume of a given mass of any gas, then,

$$V \propto \frac{1}{P} \text{ (when the temp. is constant).}$$

Charles' law states that *pressure remaining constant, the volume of a given mass of any gas increases or diminishes by 1/273rd part of its volume at 0°C. for an increase or decrease in temperature of 1°C.*

Mathematically expressed, if V_o be the volume at $0°C.$, V be the volume at $t°C.$ and V_1 the volume $t_1°C$,

$$\text{then, } V = V_o\left(1+\frac{t}{273}\right) \text{ and } V_1 = V_o\left(1+\frac{t_1}{273}\right)$$

$$V = V_o\left(\frac{273+t}{273}\right) \quad \text{and } V_1 = V_o\left(\frac{273+t_1}{273}\right)$$

Now $(273+t°)=T°$ absolute and $(273+t_1°)=T_1°$ absolute.

$$\text{Hence } \frac{V}{V_1} = \frac{273+t}{273+t_1} = \frac{T}{T_1}.$$

Thus, otherwise stated, Charles' law is

Pressure remaining constant, the volume of a given mass of any gas varies directly as its temperature on absolute scale.

$$V \propto T, \text{ when } P \text{ is constant (Charles' law)}$$

$$\text{and } V \propto \frac{1}{P}, \text{ when } t \text{ and hence } T \text{ is constant (Boyle's law).}$$

$$\therefore \quad V \propto \frac{T}{P}, \text{ when both } P \text{ and } T \text{ vary (Law of variation).}$$

$$\therefore \quad V = K\frac{T}{P}, \text{ where } K \text{ is a constant.}$$

$$\therefore \quad \frac{PV}{T} = K = \text{constant.}$$

By Boyle's and Charles' laws, we have

$$\frac{P \times V}{T} = \frac{P_1 \times V_1}{T_1},$$

where P, V and T are one set of corresponding pressure, volume and temperature, and P_1, V_1 and T_1 are another set of corresponding pressure, volume and temperature for a given mass of any gas. Then, we have

$$\frac{1000 \times 760}{273 + 27} = \frac{V_1 \times 1520}{273 + 327}, \text{ where } V_1 \text{ is the volume sought,}$$

$$\therefore \quad V_1 = \frac{1000 \times 760 \times 600}{300 \times 1520}$$

$$= 1000 \text{ c.c.}$$

Q. 3. *Alternative :—*

(*a*) *State Faraday's laws of electrolysis and express them in the form of an equation.*

(*b*) *A current of 5 amperes is passed through a copper voltameter and a silver voltameter connected in series for 32 minutes and 10 seconds. Calculate the amount of copper and silver deposited. Given electro-chemical equivalent of Cu = 0·000325g. and of silver = 0·001118g.*

Ans. (*a*) Faraday's Laws of Electrolysis are two in number.

First Law :—*The mass of an ion, liberated during electrolysis, is directly proportional to the quantity of electricity which flows through the electrolytic cell.*

If W be the mass in gm of an ion liberated by a current c amperes flowing for t seconds through an electrolytic cell and Q be the quantity of electricity in coulomb, then $W \propto Q$ or $W = Z \times Q$, where Z is a constant.

But $Q = c \times t$ where c = current in amperes and t = time in seconds.

$$\therefore \quad W = z \times c \times t.$$

Now, if $Q = 1$ (*i.e.*, $c = 1$ and $t = 1$), then $Z = W$ = mass of ion liberated by unit quantity of electricity, *i.e.*, 1 ampere flowing for 1 second. This Z is called the Electro-chemical equivalent of the liberated ion.

Second Law :—*When the same quantity of electricity flows through several electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.*

From the second law it follows that the electro-chemical equivalent (denoted by $E.\ C.\ E.$) of an element is directly proportional to its chemical equivalent. Thus

$$\frac{E.\ C.\ E.\text{ of an element }A}{E.\ C.\ E.\text{ of an element }B}=\frac{C.\ E.\text{ of }A}{C.\ E.\text{ of }B}$$

Therefore,

$$\frac{E.\ C.\ E.\text{ of any element}}{E.\ C.\ E.\text{ of Hydrogen}}=\frac{C.\ E.\text{ of the element}}{C.\ E.\text{ of }H}$$

$$=C.\ E.\text{ of the element}$$
$$(\text{because } C.\ E.\text{ of }H=1).$$

$$\therefore\ E.\ C.\ E.\text{ of any element}=\text{Its }C.\ E.\times E.\ C.\ E.\text{ of hydrogen.}$$

From the 1st law, we deduce the relationship $W=Z.\ c.t.$,

where W = mass in grams of an ion liberated ;
Z = electro-chemical equivalent of the ion ;
c = strength of the current in amperes ;
t = time measured in seconds.

From the 2nd law, we get the relationship, electro-chemical equivalent of an element (or ion).

= Electro-chemical equivalent of hydrogen × chemical equivalent of the element (or ion).

Hence, by combining these two laws, we get the mathematical relationship.

$W=H\times E\times c\times t$, where
W = mass of an element (or ion) in grams liberated ;
H = electro-chemical equivalent of hydrogen ;
E = chemical equivalent of the element (or ion) ;
c = strength of the current in amperes ;
t = time measured in seconds.

(*b*) Amount of copper liberated in the copper voltameter

$= 0{\cdot}000325 \times 5 \times 1930g$, since 32 mins. 10 secs. = 1930 secs.
$= 3{\cdot}13625g$.

Amount of silver deposited in the silver voltameter
$= 0{\cdot}001118 \times 5 \times 1930g$.
$= 10{\cdot}7887g$.

Q. 4. *Describe the preparation and properties of sulphuric acid. What is the action of hot concentrated sulphuric acid on copper, carbon, and hydriodic acid ? Give equations.*

Ans. Sulphuric acid is prepared in the laboratory by the oxidation of sulphur dioxide by atmospheric oxygen in presence of steam and nitric oxide.

In this reaction nitric oxide serves as the catalytic agent. It acts as the oxygen carrier, that is, it takes up oxygen from air forming nitrogen peroxide and gives up this oxygen to sulphur dioxide and oxidises it, nitric oxide being regenerated.

$$2NO + O_2 = 2NO_2$$
$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

According to present-day view-point, the catalytic agent is not NO but N_2O_3 or rather nitrous acid, HNO_2.

Preparation of H_2SO_4 in the laboratory.—A large flask is taken, fitted with a rubber stopper through which five glass tubes pass ; four of these tubes reach near the bottom of the

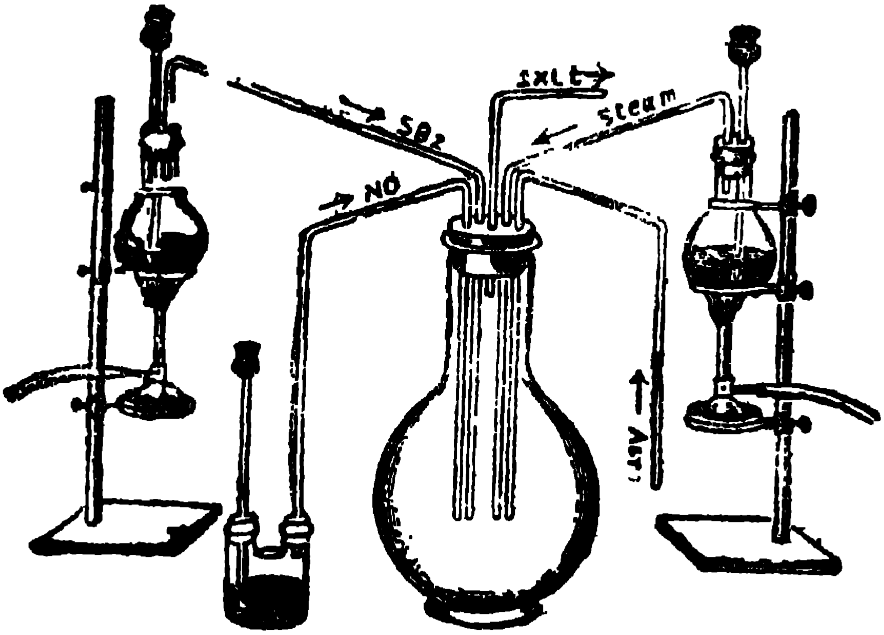


Fig. 90

flask, while the fifth is a short tube passing through the centre of the cork and serving as exit tube.

Sulphur dioxide is generated in a flask by gently heating Cu-turnings with concentrated sulphuric acid and the exit tube is connected by a rubber tube to one of the tubes fitted to the large flask.

Nitric oxide is prepared in a Woulfe's bottle by the action of moderately dilute HNO_3 on Cu-turnings and the exit tube of this generator of NO is connected to another tube fitted to the rubber stopper of the large flask. Steam is obtained by boiling water in a flask and is allowed to pass in the large flask by connecting it to yet a third tube fitted to the large flask. Dry air is introduced through the fourth tube fitted to the large flask by blowing in dry air with the help of foot blowers.

As gases enter the large flask along with steam, H_2SO_4 is formed and collects as an oily liquid at the bottom of the flask.

The unreacted gases escape through the exit tube. If the supply of steam be insufficient, white crystals having the composition $SO_2(OH)NO_2$ are found to be deposited on the walls of the flask. These are called *chamber crystals*, and these change to sulphuric acid as soon as excess of steam is supplied.

$$2SO_2(OH)NO_2 + H_2O = 2H_2SO_4 + \frac{NO + NO_2}{\text{or } N_2O_3}.$$

On an industrial scale this method is operated in the chamber process. Sulphur dioxide is produced in pyrites burners by burning iron pyrites in excess of air therein.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The hot gases from the pyrites burners are next made to enter nitre ovens where sodium nitrate is heated with conc. sulphuric acid to give rise to nitric acid vapour and oxides of nitrogen. Next the gaseous mixture of SO_2, air, HNO_3 vapour and oxides of nitrogen is made to enter a tower, known as Glover's tower, at the bottom. The tower is packed with flint or lumps of quartz. A mixture of (*i*) weak sulphuric acid from lead chambers and (*ii*) nitrated sulphuric acid from the bottom of Gay-Lussac's tower is pumped up to the top of Glover's tower and is allowed to trickle down the tower. From Glover's tower, where the gas-mixture is cooled and partly converted into

H_2SO_4, the gas-mixture is next allowed to enter lead chambers, 3 or 5 in number, made of sheet lead connected together by fusing the edges by means of oxy-hydrogen flame and kept suspended from a frame-work of wood. Cold water spray is introduced into these chambers from the roof. The gases that escape from the last chamber are made to pass up another tower, known as Gay-Lussac's tower, packed with coke and down which conc. H_2SO_4, placed in a tank above the tower, trickles. This conc. H_2SO_4 absorbs nitrous fumes. Afterwards the exhaust-gases are made to pass out by a chimney set at the end of the system.

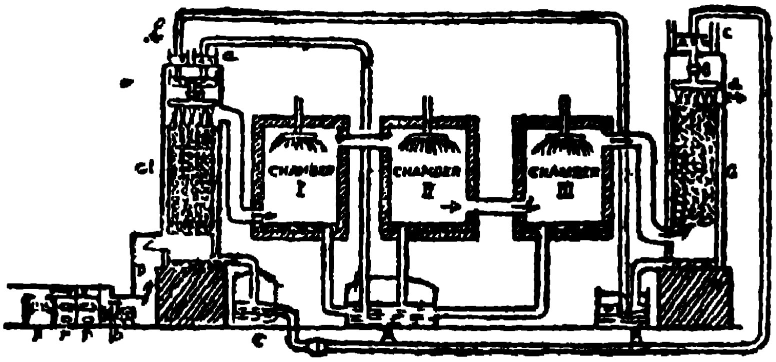


Fig. 91

The reactions that occur in the lead chambers can be represented as :

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$$
$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO$$
$$2NO + O_2 = 2NO_2.$$

Properties of sulphuric acid—It is a colourless, heavy, oily liquid of sp. gr. 1·8. It boils at 338°C.

When sulphuric acid is mixed with water, heat is evolved, so much so that steam issues out of the liquid. Hence in diluting sulphuric acid, the acid should be added, a little at a time, to water with constant stirring. Sulphuric acid has a strong affinity for water and can abstract elements of water from organic substances. Thus, formic acid decomposes by treatment with hot H_2SO_4, giving CO ; $HCOOH - H_2O = CO$. Similarly, ethyl alcohol gives ethylene : $C_2H_5OH - H_2O = C_2H_4$.

Starch, sugar, wood, paper, etc., are charred by the acid due to the separation of carbon by the removal of water :

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} - 11H_2O = 12C.$$

When strongly heated sulphuric acid decomposes into sulphur dioxide, oxygen and water.

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

Hence, hot, strong sulphuric acid sometimes acts as an oxidising agent. It oxidises carbon, sulphur, HBr and HI, itself being reduced to SO_2 : $S + 2H_2SO_4 = 3SO_2 + 2H_2O$.

$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$. It is a dibasic acid and forms normal and acid salts.

Sulphuric acid reacts with most of the metals, except gold and platinum. Cold and dilute H_2SO_4 dissolves readily zinc, iron, magnesium, evolving hydrogen and forming sulphate of the metal. Hot and concentrated H_2SO_4 dissolves copper, mercury and lead with evolution of SO_2 and formation of the sulphate of the metal.

$$Mg + H_2SO_4 = MgSO_4 + H_2$$
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Sulphuric acid can displace nitric acid from nitrates, hydrochloric acid from chlorides, phosphoric acid from phosphates, etc.

When copper is heated with conc. H_2SO_4, copper sulphate is formed, sulphur dioxide and steam being evolved.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Small quantities of sulphur trioxide are also evolved during heating, which make the sulphur dioxide evolved appear foggy inside the flask. The residue left in the flask is copper sulphate but it is always black due to its partial reduction into copper sulphide.

When carbon in the form of charcoal is heated with concentrated sulphuric acid, C is oxidised to carbon dioxide and sulphuric acid is reduced to SO_2.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$

Hot and concentrated H_2SO_4 oxidises hydriodic acid to iodine, itself being reduced to SO_2, S and even sometimes to H_2S.

$$2HI + H_2SO_4 = 2H_2O + SO_2 + I_2$$
$$6HI + H_2SO_4 = S + 3I_2 + 4H_2O$$
$$8HI + H_2SO_4 = H_2S + 4H_2O + 4I_2.$$

Q. 4. *Alternative :—*

Describe the extraction of copper from copper pyrites giving equations. State the properties and uses of copper.

Ans. Copper pyrites, Cu_2S, Fe_2S_3, contains generally only 4 to 5% of copper. So a preliminary concentration of the ore is to be carried out for enriching the ore with regard to copper-content. Otherwise the thermal treatment of the ore will cause too much waste of fuel. The usual method employed for concentrating the ore is known as *oil-floatation process.* In this process the ore is first crushed and finely powdered. The powdered ore is next added to water containing a little pine oil, xanthate and lime and the mixture is churned by blowing air through it. By this operation a froth is produced, which carries up along with it the particles of copper ore, these being preferentially wetted by oil, leaving sand and other impurities at the bottom, since these are preferentially wetted by water. The froth is collected by skimming and allowed to settle. By this means the amount of copper in the ore is raised to 30—35%.

The concentrated ore is next *roasted* in multiple-hearth furnace, the hearths being erected one above the other, so that the ore gradually descends from hearth to hearth. By this operation some of the sulphur in the ore is burnt to sulphur dioxide which escapes as gas and the metals, *viz.* iron present in the ore and copper are partially oxidised.

$$Cu_2S, Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S, Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$

the last reaction occurring only to a very small extent.

The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water jacketed blast furnace when the little quantity of Cu_2O formed in the previous operation reacts with the unchanged iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced during roasting operation reacts with sand or silica, giving a slag of ferrous silicate in the molten condition.

$$FeO + SiO_2 = FeSiO_3.$$

The slag is removed and the residue obtained, consisting of cuprous and ferrous sulphides and known as *matte*, is transferred in molten condition directly into a converter of the Bessemer type. There it is mixed with a little sand and treated with a blast of air blown through air-ports situated a little above the bottom level. This arrangement is made in order to prevent the copper formed and collected at the bottom of the converter from being oxidised by the air-blast. Iron is first oxidised to ferrous oxide, FeO, which combines with the silica of sand forming a slag of ferrous silicate as before. The slag is removed and the blast continued, whereby Cu_2S is partially oxidised to Cu_2O. When two-thirds of the matte is thus oxidised, Cu_2O formed reacts with unchanged Cu_2S giving rise to metallic copper and sulphur dioxide. The slag is removed, the blast is stopped and the converter tilted to pour off molten copper. This copper, on cooling, is found to have a blistered appearance due to escape of sulphur dioxide and is known as "*blister copper*".

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

Blister copper is then refined either (*i*) by a thermal method or (*ii*) by electrolysis.

(*i*) The *thermal refining* is carried out by melting down the blister copper on the bed of a reverberatory furnace provided with a silica lining and then blowing in air. Impurities like Fe, As, S, Pb, etc. are oxidised. Some of the oxides escape as gases, others form a slag with silica. The slag is removed. The molten mass left on the hearth consists of copper with a little cuprous oxide, Cu_2O. To reduce the latter, which makes copper brittle, anthracite coal, in the form of dust, is sprinkled on the surface of the molten mass, which is next stirred with a pole of green wood. When the copper reaches the proper tough-pitch, it is poured out.

(*ii*) *Electrolytic refining* is carried out by taking a bath of copper sulphate solution acidified with dilute sulphuric acid arranged in lead-lined wooden vats and then suspending thick sheets of impure copper from a copper-rod which is attached to the positive pole of a battery and in between thick sheets, thin plates of pure copper also hung from another copper rod connected to the negative pole of the same battery. Thick sheets of impure copper thus become the anodes in the bath and thin plates become the cathodes. On passing electric current, thick sheets gradually dissolve and pure copper is deposited on thin plates, while the impurities present in impure copper either collect at the bottom of the anodes (known as *anode-slimes*) or remain in solution.

In this way 99·99% pure copper is obtained.

Properties of copper :—Copper is a metallic element with a peculiar red colour. It is soft, malleable and ductile. It has a specific gravity of 8·85. It is very tough. It melts at 1083°C. It is a good conductor of heat and electricity.

Copper is not acted upon by dry air, but when exposed to moist air it is covered with a brownish-grey film of oxide or sulphide and after a prolonged exposure a green coating of basic sulphate of copper is formed on the surface. When heated in air, particularly at the temperature of the oxy-hydrogen flame, it burns giving cupric oxide mainly. Water has no action on pure copper at any temperature. Copper dissolves in nitric acid of all concentrations forming copper nitrate and evolving oxides of nitrogen.

$$3Cu + 8HNO_3 \underset{\text{dilute)}}{\text{(moderately}} = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O.$$

Dilute HCl has no action on copper and dilute H_2SO_4 also has no action on the metal in absence of air. Conc. H_2SO_4 has no action on the metal in the cold ; but when heated copper dissolves, forming copper sulphate and evolving sulphur dioxide as gas.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Hot concentrated HCl slowly dissolves finely-divided copper in presence of air. When HCl gas is passed over heated metallic copper, Cu_2Cl_2 (cuprous chloride) is formed and Hydrogen gas is evolved.

Uses of copper :—Copper is used largely in electric industry—

in electro-typing, for cables and wires for conveying electric current ; in the preparation of household utensils, for coinage and for the preparation of important alloys like brass, bronze, German silver, etc.

Q. 5. *What are the allotropic modifications of phosphorus ? Describe the preparation, properties and uses of red phosphorus. How can Orthophosphoric acid be prepared from red phosphorus ?*

Ans. Phosphorus exists in different allotropic modifications of which the most important are :

(1) Ordinary, white, or yellow phosphorus ; and

(2) Red phosphorus. **Preparation :**

Red phosphorus is prepared by heating white phosphorus in a covered cast iron vessel provided with a safety tube, out of contact with air, at a temp. of 240° – 250° in presence of a trace of iodine. The solid so obtained is first ground to powder with water and then boiled with caustic soda solution to remove any unchanged white phosphorus. It is then finally washed with water and dried.

Properties of red phosphorus :—Red phosphorus is a chocolate solid. It has a specific gravity of 2·2. It has no taste or smell and does not glow in the dark. It is non-poisonous. It melts at 500° – 600°C. when heated under pressure. It is insoluble in carbon disulphide and in water. It is a feeble conductor of electricity. Red phosphorus is chemically less active than ordinary white phosphorus. Heated in air, it catches fire at about 240°C. with the production of phosphorus pentoxide. It combines with the halogens and sulphur, but less energetically than the white form. It burns in chlorine only when heated and unlike the white variety, in contact with iodine it does not inflame. When strongly heated out of contact with air, red phosphorus is vaporised and the vapour on cooling condenses into white phosphorus. It is unacted upon by KOH or NaOH solution.

Uses of Red phosphorus :—Red phosphorus is used in the laboratory preparation of HBr and HI, in the manufacture of safety matches and for producing vacuum in electric lamps.

Red P is boiled with conc. HNO_3, diluted with an equal volume of water. After phosphorus has completely dissolved, the liquid is taken in a platinum dish and evaporated on a sand bath with a little more of conc. HNO_3 to oxidise any phosphorous acid, H_3PO_3, that may be formed, into H_3PO_4. The residue is evaporated at 180° to a syrupy consistency and the solution is placed in a vacuum desiccator over conc. H_2SO_4 in a dish and the desiccator is placed in a freezing mixture. Crystals of pure Orthophosphoric acid are slowly deposited.

$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

SECOND PAPER

Q. 1. *State the relationship between the atomic weight, equivalent weight, and valency of an element.*

0·1755 gram of a bivalent metal and 0·1316 gram of a trivalent metal when separately placed in dilute hydrochloric acid yielded the same volume of hydrogen gas., viz.. 190 c.c. at 27°C. and 720 mm. pressure. Find the equivalent and atomic weights of the metals.

What are the metals likely to be ?

Ans. Atomic weight of an element = Its equivalent weight × its valency.

Let V c.c. be the volume of hydrogen evolved at N.T.P. Then, by Boyle's and Charles' laws, we have

$$\frac{190 \times 720}{273 + 27} = \frac{V \times 760}{273},$$

$$\text{whence } V = \frac{190 \times 720 \times 273}{300 \times 760} \text{ c.c.} = 163{\cdot}8 \text{ c.c.}$$

Hence, weight of hydrogen displaced = 163·8 × 0·00009 gram
= ·014742 gram.

Therefore, equivalent weight of the bivalent metal =

$$\frac{0{\cdot}1755}{0{\cdot}014742} = 11{\cdot}91.$$

Hence, the atomic weight of the bivalent metal $= 11{\cdot}91 \times 2 = 23{\cdot}82$.

Also, equivalent weight of the trivalent metal $= \frac{0{\cdot}1316}{0{\cdot}014742}$ $= 8{\cdot}92$ and its atomic weight $= 8{\cdot}92 \times 3 = 26{\cdot}76$.

Bivalent metal is probably magnesium (Atomic weight $= 24{\cdot}32$) and the trivalent metal is probably aluminium (Atomic weight $= 26{\cdot}97$).

Q. 1. *Alternative :—*

Explain what is meant by the terms : Normal acid or normal alkali solution, titratian, and neutralisation.

0·3368 grams of a metal when added to 73 c.c. of distilled water produced 190 c.c. of hydrogen gas at 27°C. and 720 mm. pressure and the solution became alkaline.

Calculate the equivalent weight of the metal and the strength of the alkaline solution in terms of normality.

Guess what the metal is.

Ans. Normal acid or normal alkali solution is such a solution one litre of which contains one gram-equivalent of the acid or one gram-equivalent of the alkali dissolved in it, the gram-equivalent of acid being that weight of it which contains 1 gram of replaceable hydrogen and the gram-equivalent of alkali being that weight of it which can neutralise 1 gram-equivalent of acid.

Titration is the operation by which the strength of an unknown solution is determined by allowing it to react with a standard solution.

By neutralisation we mean the reaction between an acid and a base in solution when the two are brought in contact with each other with the production of water and salt only.

In the light of the ionic theory, neutralisation is the process of combination of H^+ – ions of an acid with the $(OH)^-$ – ions of an alkali with the formation of undissociated molecules of water.

$$H^+ + OH^- = H_2O.$$

190 c.c. of hydrogen gas at 27°C. and 720 m.m. pressure = 163·8 c.c. at N.T.P. (See answer to Q. 1 given before.)

Its weight = 163·8 × 0·00009 gram = 0·014742 gram.

$$\text{Therefore, equivalent weight of the metal} = \frac{0{\cdot}3368}{0{\cdot}014742} = 22{\cdot}84$$

Since 73 c.c. of the solution produced contain 0·3368, grams of the metal, 1000 c.c. of the solution contain

$$\frac{0{\cdot}3368 \times 1000}{73} \text{ grams of the metal.}$$

Again, since equivalent weight of the metal is 22·84, the

$$\text{strength of the solution} = \frac{0{\cdot}3368 \times 1000}{73 \times 22{\cdot}84}(N) = 0{\cdot}202(N).$$

Since the solution is alkaline after the evolution of hydrogen, the metal is either an alkali metal or an alkaline earth metal. The metal is most probably the alkali metal sodium, when the equivalent weight becomes equal to its atomic weight, the valency of sodium being one. The atomic weight of sodium is 22·997, very near to, 22·84. If it be an alkaline earth metal with valency 2, the atomic weight of such a metal would be 22·84 × 2 = 45·68, a value to which no alkaline earth metal corresponds.

Q. 2. *Make a diagrammatic sketch of the Kipp's Apparatus that you have yourself used or that you have seen being used in a chemical laboratoy. Explain how the device of this apparatus enables one to get either a continuous or an intermittent supply of hydrogen sulphide gas ?*

Illustrate the usefulness of this gas as an analytical reagent. How would you determine the composition of the gas ?

Ans. The device of this apparatus helps us in getting a continuous supply of hydrogen sulphide by allowing the acid to remain in contact with ferrous sulphide placed in the middle globe.

$FeS + H_2SO_4 = FeSO_4 + H_2S.$

When the gas is not required, the stop-cock of the exit-tube fitted to the middle globe is closed ; the gas that collects in the middle globe exerts pressure on the acid present therein, and thereby forces the acid out of the central globe. The acid rises up the stem and goes to the top-most globe. Thus the contact between acid and ferrous sulphide is broken and the reaction giving H_2S stops. When the gas is required, the stop-cock of the exit-tube is opened, H_2S present in the central globe comes out, the acid comes down from the top-most globe and again comes in contact with the ferrous sulphide in the middle globe, thus supplying H_2S again by their interaction.

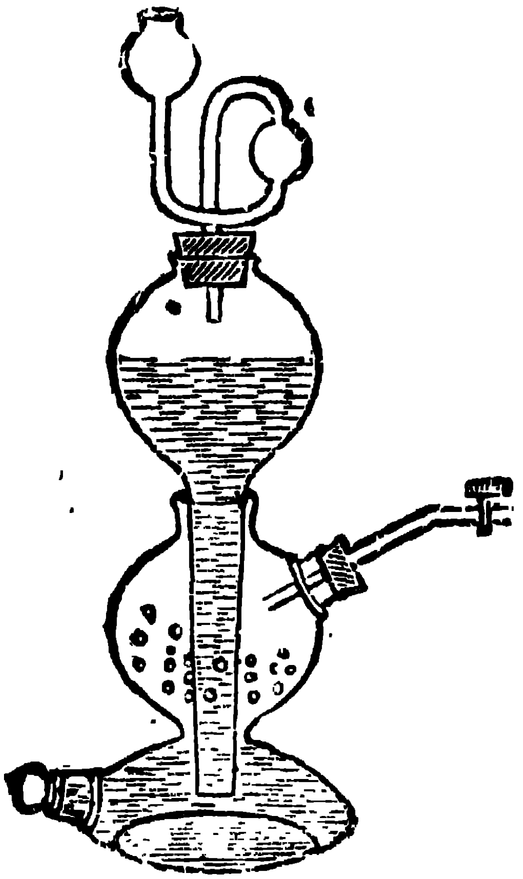


Fig. 92

H_2S as an analytical reagent :—

Sulphuretted hydrogen is a very valuable chemical reagent in the laboratory. It is employed for (1) identifying some metals in solution of their salts. (2) classifying metals into groups according to the behaviour of their sulphides towards acids, alkalies and water and (3) separating metallic radicals from one another in a mixture.

(1) When H_2S is passed through solutions of salts of some metals, their sulphides are precipitated. These sulphides are of characteristic colour and the colour of the precipitate shows which metal we are dealing with. Thus, orange ppt. by passing H_2S indicates an antimony salt ; yellow ppt. indicates either cadmium or arsenic or a stannic salt ; white ppt. indicates a zinc salt.

(2) Metals can be broadly divided into three groups according to the solubilities of their sulphides in water, ammonia and acids :—

(*a*) Metals whose sulphides are insoluble in the dilute acids and can, therefore, be precipitated from a solution of their salts containing dilute acids, *e.g.*, copper, mercury, lead, arsenic, etc.

(*b*) Metals whose sulphides are soluble in dilute acids but insoluble in water and in ammonia and can, therefore, be precipitated from ammoniacal solution of their salts, *e.g.*, iron, zinc, manganese, etc.

(*c*) Metals whose sulphides are soluble in water (not to speak of alkalies and acids) and cannot, therefore, be precipitated at all by H_2S, *e.g.*, calcium, potassium, and magnesium.

(3) Now, if we have a mixture of salts of metals belonging to each of the above three groups, we can separate these metallic radicals, with the help of H_2S. Thus a mixture of copper sulphate, zinc sulphate and sodium chloride being given, the solution is acidified with dil. HCl. heated to boiling, and H_2S passed in when black copper sulphide is precipitated. The ppt. is filtered off after complete precipitation, ammonia is added to the filtrate till the solution is alkaline and more H_2S is passed in, when white zinc sulphide is precipitated. The white ppt. is filtered off when the precipitation is complete. The filtrate contains the sodium salt. Thus the three metallic radicals are separated from one another.

The composition of hydrogen sulphide is established in the following ways :—

A thumb-tube is completely filled with mercury and inverted over mercury placed in a trough. A few cubic centimetre of dry hydrogen sulphide is collected in the tube by displacement of mercury. The position of the mercury level in the tube is carefully marked by means of a rubber ring. A piece of metallic tin is introduced through the bottom of the tube, the tube is closed with the thumb and by a jerking motion given to the tube, the bit of tin is taken into the horizontal portion

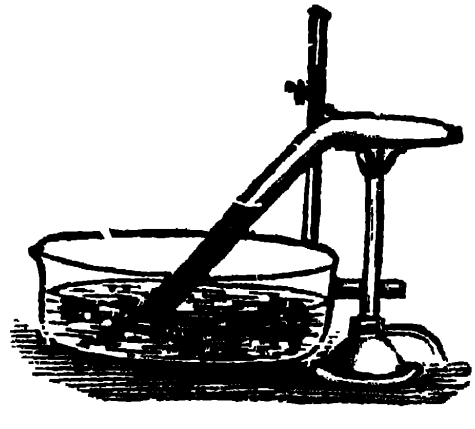


Fig. 93

of the tube. The tube is then placed in the mercury in the trough and kept fixed to a retort stand by a suitable clamp. The bit of tin is then heated by a burner from outside. Tin combines with sulphur of hydrogen sulphide, forming tin sulphide and liberating hydrogen. When the reaction is over, the tube is allowed to cool to the room temperature and the position of the mercury level inside the tube is noted. It is found that the mercury stands at the same level as before. The residual gas is proved to be hydrogen by the facts that it burns with a scarcely visible blue flame with the production of water only and is absorbed by heated metallic palladium. Hence the volume of hydrogen produced is equal to the volume of hydrogen sulphide decomposed, or, in other words, hydrogen sulphide contains its own volume of hydrogen.

Then we have, 1 volume of hydrogen sulphide contains 1 volume of hydrogen. Let "*n*" be the number of molecules present in each volume of gas. Therefore *n* molecules of hydrogen sulphide contain *n* molecules of hydrogen (Avogadro's hypothesis). Hence, 1 molecule of hydrogen sulphide contains 1 molecule or 2 atoms of hydrogen, since hydrogen molecule is diatomic (Deduction from Avogadro's hypothesis). Thus the formula for hydrogen sulphide is H_2S_x, where x is an integer. Now, the density of hydrogen sulphide is 17 (experimental) and so its molecular weight is $2 \times 17 = 34$ (Deduction from Avogadro's hypothesis).

Now, of the 34 parts by weight of hydrogen sulphide, 2 parts are accounted for by 2 atoms of hydrogen ; the remaining 32 parts are to be accounted for by x atoms of sulphur. Now 32 is the atomic weight of sulphur and 32 parts can stand for only one atom of sulphur. Therefore $x = 1$, and the molecular formula for hydrogen sulphide is H_2S.

Q. 2. *Alternative :—*

Make a diagrammatic sketch of a sulphuric acid chamber plant or of a laboratory experiment illustrating the chamber process. Indicate on your diagram the name, contents and function of each part of the plant or apparatus.

Give the chemical reactions of the process as far as you can.

Ans.

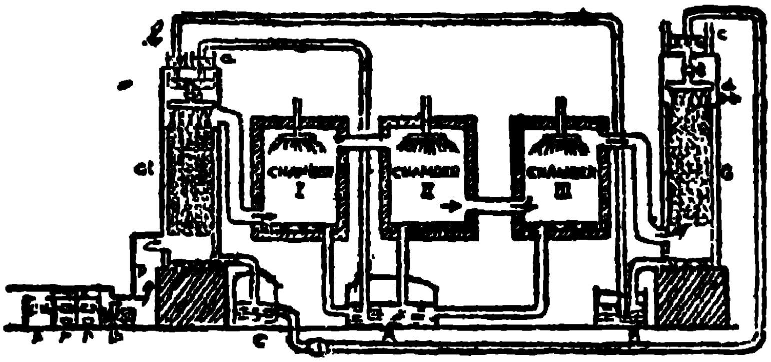


Fig. 94

ppp.—pyrites or sulphur burners.

p = nitre pots, in which sodium nitrate and conc. H_2SO_4 are heated together.

Gl = Glover's tower, packed with flints.

b = pipe by which nitrated acid from Gay Lussac's tower is pumped up to Glover's tower..

c = pipe by which chamber acid is pumped up to Glover's tower.

I, II, III = Lead chambers into which steam is injected from above.

G = Gay Lussac's tower, filled with coke.

Functions of Glover's tower :—

(1) To cool the hot gaseous mixture from pyrites burners and nitre pots.

(2) To concentrate the chamber acid.

(3) To denitrate the nitrated acid from Gay Lussac's tower.

(4) To help in producing H_2SO_4 from the gaseous mixture, SO_2, HNO_3 and water vapour.

Functions of the chamber :

(1) To produce H_2SO_4 from the gas mixture and steam injected into it.

Function of Gay Lussac's tower :—

(1) To absorb the oxides of nitrogen escaping from the chambers in conc. H_2SO_4 trickling down the chamber.

Reactions of the chamber :—

(1) $SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$.

(2) $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$.

(3) $2NO + O_2 = 2NO_2$.

When the steam falls short, the following reactions take place :

(1) $3NO_2 + 2SO_2 + H_2O = NO + 2SO_2(OH)(NO_2)$ chamber crystals.

(2) $2SO_2(OH)(NO_2) + H_2O = 2H_2SO_4 + N_2O_3$.

(3) $N_2O_3 = NO_2 + NO$. (4) $2NO + O_2 = 2NO_2$.

For diagrammatic sketch of a laboratory experiment illustrating chamber process for the manufacture of H_2SO_4 see Fig. 90, Q. 4, First Paper, 1952, where chemical reactions of the process is also given. The different parts have also been labelled.

Q. 3. *Make out a table of the chief physical and chemical properties of the elements of the chlorine family and point out the striking features about them.*

Ans. Fluorine, chlorine, bromine and iodine, these four elements are called the *halogens*, which means sea-salt producer. This name is applied to these elements because the compounds produced by the union of these elements with sodium resemble sea-salt (sodium chloride).

Comparison of the Physical Properties of the Halogens :

Properties	Fluorine	Chlorine	Bromine	Iodine
(1) State of aggregation.	Gas	Gas	Liquid	Solid
(2) Colour of vapour.	Pale greenish yellow.	Greenish yellow.	Brownish red.	Violet
(3) Odour.	Irritating.	Irritating and pungent.	More irritating than that of chlorine.	Less marked smell than that of chlorine or Bromine.
(4) Heaviness or specific gravity.	Slightly heavier than air.	$2\frac{1}{2}$ times heavier than air.	Sp. gr. 3·19 (liquid.)	Sp. gr. 4·9 (solid).
(5) Solubility in water.	Decomposes water with evolution of ozonised oxygen.	Fairly soluble (chlorine water).	Fairly soluble (Bromine) water).	Very slightly soluble.

Comparison of the Chemical Properties of the Halogens :

Properties	Fluorine	Chlorine	Bromine	Iodine
(1) Reaction with H_2	Unites readily with H_2 even in the *dark* with explosion with the formation of HF which is stable. $H_2+F_2=2HF$	Unites readily with H_2 in *direct sunlight* with *explosion* with the formation of HCl which is less stable than HF. $H_2+Cl_2=2HCl$	Unites with H_2 only when heated with the formation of HBr which is decomposed by heat and also by Cl_2. $H_2+Br_2 \rightleftharpoons 2HBr$	Unites with H_2 when heated in presence of a catalyst with the formation of HI which is decomposed by slight heating and also by Cl_2 and Br_2. $H_2+I_2 \rightleftharpoons 2HI$
(2) Reaction with water.	Decomposes water with the formation of HF and evolution of ozonised oxygen. $2F_2+2H_2O=4HF+O_2$ $3F_2+3H_2O=6HF+O_3$.	Decomposes water when kept exposed to sunlight with the formation of HCl and evolution of O_2 $2Cl_2+2H_2O=4HCl+O_2$.	Slowly decomposes water when kept exposed to sunlight with the formation of HBr and evolution of O_2 $2Br_2+2H_2O=4HBr+O_2$.	No action on water.
(3) *Bleaching action.*	Decomposes organic substances.	Readily bleaches vegetable colouring matter.	Bleaches more slowly than chlorine.	Possesses practically no bleaching properties.
(4) *Chemical activity*	Most active. Liberates Cl, Br, I from chlorides, bromides and iodides respectively.	Less active than fluorine displaces Br and I from bromides and iodides respectively.	Less active than chlorine. Displaces iodine from iodides.	Least active. Cannot displace F, Cl or Br from fluorides, chlorides and bromides.
(5) Compounds with oxygen.	Gives the oxide F_2O by indirect combination.	Forms several unstable oxides Cl_2O, ClO_2, Cl_2O_7 all formed indirectly.	Two oxides known Br_2O and Br_3O_8.	Gives stable oxides IO_2, I_4O_9 and I_2O_5.

Properties	Fluorine	Chlorine	Bromine	Iodine
(6) Action on starch-solution.	Attacks water of the solution.	No change in colour of starch solution.	Starch solution is coloured *yellow*.	Starch solution is coloured *blue*.
(7) Properties of compounds with Barium.	White, crystalline *insoluble*.	White, crystalline *soluble*.	White, crystalline, *soluble*.	White, crystalline, *soluble*.
(8) Properties of compounds with silver.	White *soluble*.	White *insoluble*, chemically changed by light.	Yellowish white *insoluble*, chemically changed by light.	Yellow, *insoluble*, chemically changed by light.

The striking features of the halogen family of elements are (1) their extreme reactivity, (2) their characteristic colou the vapourous state, and (3) the strong acid character of their hydrogen compounds.

Q. 3. *Alternative* :—

Describe the preparation, properties and uses of **any four** *of the following* :—

Magnesium chloride ; *Potash alum* ; *Calcium carbide* ; *Sodium peroxide* ; *Mercurous chloride* ; *Zinc oxide* ; *Plaster of Paris* ; *Iron sulphide.*

Ans. *Magnesium chloride hexahydrate,* $MgCl_2, 6H_2O$, is prepared by dissolving metallic magnesium, its oxide or carbonate in dil. HCl, filtering the solution and concentrating it to crystallisation when on cooling crystals of $MgCl_2, 6H_2O$ separate out.

$$MgCO_3 + 2HCl = MgCl_2 + CO_2 + H_2O.$$

Anhydrous magnesium chloride is prepared by heating magnesium in a current of dry hydrogen chloride or chlorine.

Properties.—It is a white deliquescent, crystalline substance soluble in water. On heating the crystals, at first five molecules of water are removed and then it undergoes partial decomposition into the oxide and hydrogen chloride.

$$MgCl_2 + H_2O = MgO + 2HCl.$$

Uses—$MgCl_2$ is largely used in dressing cotton goods. $MgCl_2$ mixed with MgO is used as a cement for broken porcelain.

Potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$—Alum is prepared from *alunite*, or alum-stone, K_2SO_4, $Al_2(SO_4)_3$, $4Al(OH)_3$ by roasting with fuel, exposing to air, lixiviating with water and then crystallising. In the laboratory it can be prepared by mixing a hot solution of aluminium sulphate in water with the requisite amount of potassium sulphate and then cooling the mixed solution, when crystals of alum separate out,

Properties.—It is a colourless, crystalline substance soluble in water. When heated, alum first melts in its water of crystallisation ; on further heating, it undergoes decomposition, leaving a white porous mass known as burnt alum.

Uses—Alum is used in dyeing industry as a mordant, in calicoprinting, in medicine and for purifying water.

Calcium carbide is manufactured by heating a mixture of lime and carbon in an electric furnace at about 2000°C. Calcium carbide is formed in the molten condition and is tapped out by the tapping hole into a tray where it sets to a slab.

$$CaO + 3C = CaC_2 + CO.$$

Properties.—It is a hard brittle crystalline solid. It reacts with water giving acetylene. $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. When heated in a current of nitrogen to about 1100°C, it forms calcium cyanamide, $CaC_2 + N_2 = CaCN_2 + C$.

Uses—It is used in generating acetylene, in the manufacture of calcium cyanamide which is used as a fertiliser and as a reducing agent.

Sodium peroxide, Na_2O_2, is prepared by heating sodium placed on aluminium trays which are pushed slowly inside in an iron tube in the opposite direction to the current of dry CO_2-free air admitted, the iron tube boing heated to 300°C.

$$2Na + O_2 = Na_2O_2.$$

Properties.—It is a yellowish-white powder. When exposed to moist air, it absorbs moisture and carbon dioxide. $2Na_2O_2 +$

$2CO_2 = 2Na_2CO_3 + O_2$. It dissolves in water, forming NaOH and O_2.

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

If the temperature be kept low, hydrogen peroxide is produced.

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2.$$

With dilute acids in the cold, hydrogen peroxide is formed and salts of sodium are produced,

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

Uses.—It is used in the manufacture of hydrogen peroxide, for the preparation of oxygen and as an oxidising agent in the laboratory.

Mercurous chloride, also known as calomel, is prepared by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel when Hg_2Cl_2 formed sublimes off and condenses as a white cake in the upper cooler part of the vessel. The sublimate is collected and repeatedly boiled with water and filtered inorder to free it completely from any adhering mercuric chloride. It is then dried and sent out to the market. $HgCl_2 + Hg = Hg_2Cl_2$.

Properties of calomel.—It is an amorphous white powder without any taste. It is insoluble in water and in dilute acids. It sublimes without decomposition when heated. It dissolves in aqua regia forming mercuric chloride. When treated with ammonia, it turns black due to the formation possibly of a mixture of finely divided mercury and amido-mercuric chloride, NH_2HgCl.

Uses of calomel.—Calomel or mercurous chloride is used in medicine as a purgative.

Zinc oxide, ZnO, may be prepared by heating the hydroxide, nitrate or carbonate of the metal strongly is air.

$$ZnCO_3 = ZnO + CO_2.$$

It is manufactured by burning zinc in air and then condensing the fumes in suitable chambers.

$$2Zn + O_2 = 2ZnO.$$

Properties.—Zinc oxide is a white powder which turns yellow on heating, but regains its white colour on cooling. It produces a green mass when heated with a small amount of cobalt nitrate solution. It is insoluble in water but dissolves in acids producing the corresponding salts. It dissolves also in alkalies, forming Zincates.

Uses—Zinc oxide is used as a pigment. It is also used in medicine, dentistry, and in preparing *Rinmnan's green*, a pigment.

Plaster of paris, $(CaSO_4)_2, H_2O$ is prepared by heating gypsum, $CaSO_4, 2H_2O$, in a kiln or oven to a temperature of 120°—130°C, taking care that gypsum does not come into contact with carbonaceous fuel.

$$2(CaSO_4, 2H_2O) = (CaSO_4)_2, H_2O + 3H_2O.$$

Properties—It is a white powder and combines with water forming a hard mass ; this is known as setting of Plaster of Paris, and is due to reconversion into gypsum.

$$(CaSO_4)_2H_2O + 3H_2O = 2(CaSO_4, 2H_2O)$$

Uses.—Plaster of Paris is used for making moulds in pottery works, in surgical bandages, as a cement in ornamental casting and in preparing bust, statues etc.

Iron sulphide, Ferrous sulphide, FeS is prepared by heating 3 parts of iron filing with 2 parts of sulphur.

$$Fe + S = FeS.$$

Properties.—When pure, it is a yellowish crystalline mass with a metallic lustre. The commercial variety is black and contains free iron. It is insoluble in water but dissolves readily in dilute acids with the evolution of H_2S.

$$FeS + 2HCl = FeCl_2 + H_2S.$$

Uses.—It is used in the laboratory for generating H_2S in a Kipp's Apparatus.

Iron sulphide, Ferric sulphide, Fe_2S_3, is obtained by the action of H_2S on pure moist ferric hydroxide in absence of oxygen.

Properties.—It is a black solid, insoluble in water. It decomposes, especially in presence of excess of ferric salt, into a mixture of FeS and Sulphur.

Q. 4. *Describe the tests you would apply to establish the identity of the following :—*

(*i*) *A white powder that may be either white lead or zinc white.*

(*ii*) *A strip of white metal that may be either silver or tin.*

(*iii*) *A colourless solution that may contain either stannous or stannic chloride.*

(*iv*) *A colourless gas in a cylinder that may be either oxygen or ozone.*

Ans. (*i*) The white powder is taken on a charcoal groove and heated strongly at first in the oxidising flame. If the mass becomes yellow when hot and white on cooling, it may be zinc white (ZnO). If not, the residue on the charcoal groove is heated in the reducing flame when a metallic bead with a yellow incrustation is obtained. The bead is collected and dissolved in nitric acid in a test tube, the excess of acid removed by boiling and then potassium chromate added to it when a yellow precipitate is obtained showing the bead to be of metallic lead. That white powder which gives this bead of lead is white lead and the other one is therefore zinc white.

(*ii*) A little of the strip of white metal is treated with conc. HNO_3. That metal which dissolves in HNO_3 is silver. Tin is not acted upon by conc. HNO_3, but by adding a drop of water to it, vigorous reaction takes place and a voluminous white powder of metastannic acid is produced in case of metallic tin. Further, to the solution in HNO_3 obtained in the first case, if we add dil. HCl, a curdy white precipitate is obtained, insoluble in HNO_3 but soluble in NH_4OH. This confirms silver. The other one is, therefore, tin.

(*iii*) A little of the solution is added to mercuric chloride solution ; if a white ppt. be obtained, the solution is of stannous chloride, the other one is, therefore, of stannic chloride. Moreover, on passing H_2S through the solutions, that one which gives a chocolate-brown ppt. is of stannous chloride and the other which gives a yellow precipitate is of stannic chloride.

(*iv*) The stopper of the cylinder is pushed a little and the gas smelt. If fishy odour be perceptible, it is ozone. A little KI solution is then taken and the gas is passed into it. If iodine is liberated, as recognised by the reddish-brown colour of the solution, we are to infer that the gas is ozone.

Q. 5. *State what you know about the approximate composition,* *properties and uses of the three commercial forms of iron, namely cast iron, steel and wrought iron.*

Describe how cast iron is converted into steel in a Bessemer converter.

Ans. The nature of the three forms of commercial iron depends upon the amount of impurities, especially carbon, present in iron. Thus cast iron containing the highest proportion of carbon is the most impure form of commercial iron ; it contains also Si, Mn, P, S etc. as impurities. Wrought iron, containing the minimum amount of carbon and other impurities to a negligible proportion is taken as the purest form of commercial iron. Steel lies intermediate, both with regard to carbon content and other impurities, between the two other varieties.

In the following table, the approximate composition with reference to carbon content, properties and uses of the three varieties are shown.

Properties	**Cast iron**	**Steel**	**Wrought iron**
1. *Amount of carbon*	2 to 5%	0 25 to 1·5%	0·12 to 0·25%
2. *Melting point*	1200°C.	1300°—1400°C.	1500°C.
3. *Brittleness* or *malleability*	Brittle	Malleable and sometimes brittle	Malleable
4. *Hardness*	Hard	Hard and soft	Soft
5. *Tempering*	Cannot be tempered	Can be tempered	Cannot be tempered
6. *Welding*	Cannot be welded	Can be welded	Can be welded
7. *Structure*	Crystalline	Crystalline	Fibrous
8. *Magnetisation*	Cannot be permanently magnetised	Can be permanently magnetised	Cannot be permanently magnetised

Properties	Cast Iron	Steel	Wrought iron
Uses	For preparation of cast articles like ornamental railings, cast cooking utensils etc. Also employed for the manufacture of steel and wrought-iron.	In the manufacture of railway lines, locomotives, joists, cranes, etc. Employed in the manufacture of implements of husbandry and war. Also used in the production of surgical instruments, cutlery, etc. Utilised in the manufacture of artificial magnets, watch-springs etc.	In the manufacture of articles of commerce produced by hammering ; in the preparation of electromagnets piano-wires and wire-netting.

Steel is at present obtained from cast iron at the first stage by placing molten cast iron in a Bessemer Converter and then by blowing air through the molten mass. Bessemer converter is a large pear-shaped vessel made of wrought iron plates rivetted together. The vessel is mounted on trunions, so that it can be tilted in any position, either vertical or horizontal, with its help. An air-chamber is fitted to the base, and through this air-chamber a powerful blast of air can be admitted. The

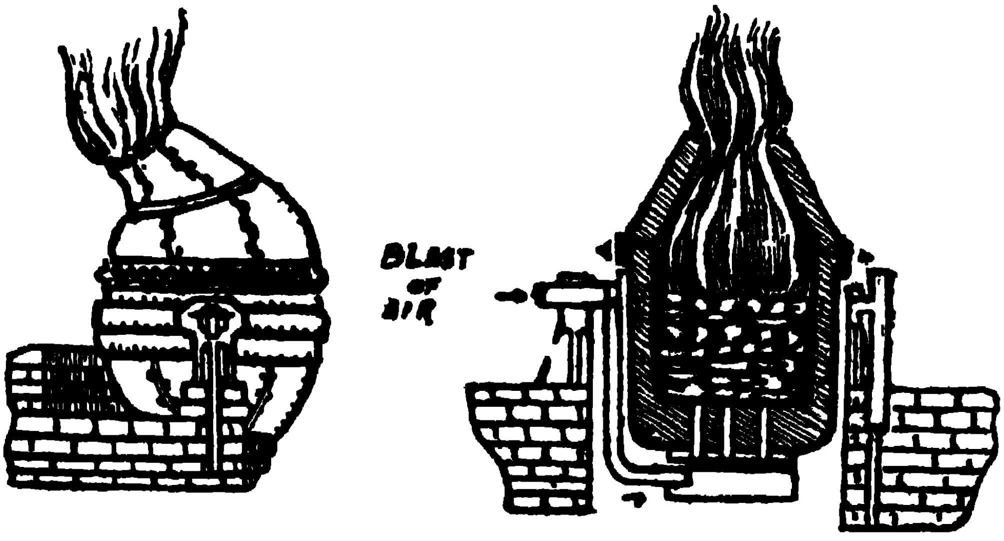


Fig. 95

converter is lined either with siliceous material (in *acid* Bessemer process) when the cast iron used in the operation is free from phosphorus, or with burnt dolomite or magnesite (in *basic* Bessemer process) when phosphorus is present as impurity in cast iron to be used in the operation.

The converter is first tilted into the horizontal position and a quantity of molten cast iron directly from the blast furnace or from a metal-mixer is run in. The blast of air is then started and the converter immediately swung back into a vertical position. Within a very short time the whole of the impurities is burnt away. The completion of the operation is sharply marked by the sudden disappearance of the flame from the open mouth of the converter. The blast is stopped at this stage in the *acid* Bessemer process, but in the *basic* Bessemer process the blast is continued for a few minutes even after the dropping of the flame and it is stated that during this after-blow phosphorus is removed. The converter is then once more tilted into a horizontal position and an exact quantity of molten *Spiegeleisen* (a mixture of C, Fe and Mn, containing about 20% Mn, shortened as *Spiegel*) is then added to recarburise the steel ; the blast of air is then turned on for a short time in order to mix the materials thoroughly. Next the contents are poured out into ladles. In case of phosphatic cast iron being used, spiegel is added after pouring the molten charge on to ladles.

1953

FIRST PAPER

Q. 1. *Define and illustrate : (a) atomic weight, (b) equivalent weight.*

0·1 grm. of a metal, of which the specific heat is 0·214, on solution in hydrochloric acid displaced 124·4 c.c. of dry hydrogen at N.T.P.

Calculate the atomic weight of the metal, and write down the formula for its oxide and chloride.

Ans. (*a*) The atomic weight of an element is a number expressing the relative weight of an atom of the element with respect to the weight of an atom of hydrogen. Thus, when we say that the atomic weight of chlorine is 35·5, we mean that the weight of one atom of chlorine is 35·5 times the weight of an atom of hydrogen.

Thus, $\frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of hydrogen}} = 35{\cdot}5.$

Hydrogen was taken as the standard in expressing the atomic weights of elements in terms of its atomic weight, because it is the lightest element known. But the hydrogen standard of the atomic weights of elements, which was strongly advocated by Proust, was to be given up on account of several complications, and in its place oxygen with an atomic weight value 16·00 has been accepted as the standard of atomic weights. On that basis, when we speak of the atomic weight of chlorine to be 35·46, we mean

$$\frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of oxygen}} \times 16 = 35{\cdot}46.$$

N.B. There is a slight difference in the atomic weight values of different elements on the hydrogen standard and on the oxygen standard, since on the basis of O = 16, H = 1·008 and not 1, as it was used in the hydrogen standard of atomic weights.

(*b*) The equivalent weight of an element is that weight of element which combines with or displaces from a compound one part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine. It is a mere number, since it can be expressed as chemical equivalent

$$= \frac{\text{wt. of the element in certain unit}}{\text{wt. of hydrogen displaced by or combined with the given wt. of the element in the same unit.}}$$

Thus 12 parts by weight of magnesium can displace 1 part by weight of hydrogen. Therefore 12 is the equivalent weight of magnesium.

Again 31·75 parts by weight of copper combine with 8 parts by weight of oxygen. Hence 31·75 is the equivalent weight of copper. Also 20 parts by weight of calcium combine with 35·5 parts by weight of chlorine. Therefore 20 is the equivalent weight of calcium.

Weight of 124·4 c.c. of hydrogen at N.T.P.
$=124{\cdot}4 \times 0{\cdot}00009$ grm.
$=0{\cdot}011196$ grm.
Therefore, equivalent weight of the metal

$$=\frac{0{\cdot}1}{0{\cdot}011196}=8{\cdot}93$$

Since the specific heat of the metal is 0·214, therefore, according to Dulong and Petit's law,

approximate atomic weight of the metal $=\frac{6{\cdot}4}{0{\cdot}214}=29{\cdot}90$

Hence, the valency of the metal $=\frac{29{\cdot}90}{8{\cdot}93}=3$

(nearest whole number)

Therefore, the exact atomic weight of the metal
$=8{\cdot}93 \times 3=26{\cdot}79$.

Since the valency of the metal is 3, its oxide shall have the formula M_2O_3 and its chloride shall have the formula MCl_3, where M stands for the metal.

Q. 2. *How could you distinguish between (a) carbon monoxide and carbon dioxide ; (b) hydrogen and methane ; (c) hydrochloric and hydrobromic acid ; (d) nitrous oxide and nitric oxide ?*

Ans. (*a*) (*i*) Carbon monoxide does not change the colour of litmus solution, but carbon dioxide turns litmus solution port-wine red. (*ii*) Carbon monoxide does not turn lime-water milky, but carbon dioxide, when shaken with lime-water, turns the latter milky. (*iii*) Carbon monoxide. when brought in contact with a lighted taper catches fire and burns with a lambent blue flame, whereas carbon dioxide under similar condition, extinguishes the lighted taper and does not itself burn. (*iv*) Carbon monoxide, when passed into caustic alkali solutions, is not absorbed, but carbon dioxide is completely absorbed by caustic alkali solutions. (*v*) When passed over heated black copper oxide, carbon monoxide reduces the oxide to red metallic copper, but carbon dioxide cannot reduce the oxide to the metal.

(*b*) (*i*) Both hydrogen and methane burn with a lambent-blue flame when set fire to in contact with air, but the product obtained in the case of hydrogen does not turn lime-water milky, whereas that obtained in the case of methane turns, lime-water milky, since carbon dioxide is produced during the burning of methane along with water, which is the only product in case of burning of hydrogen.

(*ii*) When placed in contact with palladium metal foil, hydrogen is absorbed as will be seen by the rise of mercury level in the gas-jar, if the gas be collected over mercury, but methane is not at all absorbed by metallic palladium.

(*iii*) When both hydrogen and methane are mixed with chlorine-gas in the gas-jars in the dark and the mixture is exposed to direct sunlight, explosion occurs in both cases, but in the hydrogen gas-jar no soot is deposited whereas in the gas-jar which contains methane, carbon separates in the form of soot.

(*c*) (*i*) In aqueous solution, hydrochloric acid produces a curdy-white precipitate, when treated with silver nitrate solution, of silver chloride, insoluble in nitric acid, but readily soluble in ammonia. Hydrobromic acid, under similar conditions, yields a light-yellow precipitate of silver bromide, insoluble in nitric acid and difficultly soluble in ammonia.

(*ii*) When treated with chlorine-water in presence of carbon disulphide, hydrochloric acid does not show any change, but carbon disulphide layer is coloured brown in case of hydrobromic acid, due to separation of bromine which dissolves in CS_2 producing the brown solution.

(*iii*) When shaken with chlorine-water and starch, hydrochloric acid shows no change in colour, whereas in the case of hydrobromic acid the solution turns orange-yellow in colour.

(*d*) (*i*) When a glowing chip of wood is introduced into a jar of nitrous oxide gas, the glowing chip bursts into flame, but when introduced into a jar of nitric oxide the glowing chip is not rekindled.

(*ii*) When exposed to air nitric oxide alone forms brown fumes with oxygen of air, due to formation of nitrogen peroxide, but nitrous oxide does not give any brown fumes.

(*iii*) When shaken with a little carbon disulphide, the mixture of nitric oxide and carbon disulphide vapour burns when ignited with a blue flame, but nitrous oxide does not behave in the same way.

(*iv*) When shaken with ferrous sulphate solution (colourless) nitric oxide turns the colour of the solution brown, due to the formation of a loose compound, $FeSO_4$, NO, but nitrous oxide shows no change in colour.

Q. 2. *Alternative* :

Write short explanatory notes on :—(*a*) *Atoms and molecules* ; (*b*) *Oxidation and reduction* ; (*c*) *Chemical and physical changes* ; *and* (*d*) *Catalytic agent.*

Ans. (*a*) **Atoms** : An atom of an element is the smallest particle of that element which can take part in a chemical change. According to **Dalton's atomic theory**, atoms are incapable of further division, and they can neither be created nor destroyed. Usually atoms of elements are found incapable of separate existence, but in some cases, as of inert gases of argon family, which possess monatomic molecule, atoms of those elements are found to exist in the free state.

Molecules : A molecule of any substance, either elementary or compound, is the smallest particle of that substance, which can exist in the free state preserving all characteristics of that substance. Molecules are made up of one or more atoms of the same element (in the case of elementary substances) or two or more atoms of different elements (in the case of compounds).

Thus a molecule of mercury or sodium in the vapourous state consists of only one atom of the particular element ; the molecule of hydrogen, oxygen or nitrogen (elementary gaseous substances) consists of 2 atoms each of the element concerned ; a molecule of hydrochloric acid and of steam (compound vaporous substances) consists of 2 atoms and 3 atoms respectively of different elements. A molecule of calcium carbonate (a solid compound) consists of 5 atoms, viz., 1 of calcium, 1 of carbon and 3 of oxygen.

(*b*) **Oxidation** is defined as the process which increases the proportion of oxygen or of an equivalent electro-negative element or radical in an element or a compound, or which decreases the proportion of hydrogen or of an electro-positive element or radical in a compound.

Reduction is defined as the result of the opposite operations. Thus, **reduction** is the process which increases the proportion of hydrogen or of an electro-positive element or radical in an element or a compound, or which diminishes the proportion of oxygen or of an equivalent electronegative element or radical in a compound.

Thus, when magnesium is burnt in oxygen, it combines with oxygen with the formation of its oxide. Hence magnesium is said to be *oxidised* :—$2Mg + O_2 = 2MgO$.

When iron is heated in a stream of chlorine gas, it combines with chlorine, forming ferric chloride. Iron is said to be oxidised, due to combination with an electronegative element chlorine :—$2Fe + 3Cl_2 = 2FeCl_3$.

When conc. hydrochloric acid is heated with manganese dioxide, it is oxidised to chlorine by removal of hydrogen :—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

Similarly, the following are the examples of reduction :—

CuO (red-hot) $+ H_2 = Cu + H_2O$ (removal of oxygen) from CuO.

$H_2S + I_2 = 2HI + S$ (addition of hydrogen to iodine).

$FeCl_3 + H$ (nascent) $= FeCl_2 + HCl$ (Reduction in the proportion of the electronegative element).

Among inorganic compounds, oxidation means usually an increase in the active valency of the central atom, as for example, when ferrous chloride ($FeCl_2$) is oxidised to ferric chloride ($FeCl_3$), the valency of iron increases from 2 to 3. Similarly in case of oxidation of stannous chloride ($SnCl_2$) to stannic chloride ($SnCl_4$), the valency of tin increases from 2 to 4.

From ionic standpoint, if we take into consideration the reaction,

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2,$$

it can be represented as

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised to the stannic ion by the loss of two electrons which have passed to the two ferric ions, reducing them to the ferrous state.

Hence, *oxidaton* may be defined as *a loss of electrons* and *reduction* as *a gain of electrons.*

Moreover, it must also be observed that oxidation and reduction take place simultaneously in a reaction. Whenever a substance is oxidised, another one is reduced. Thus when stannous chloride and mercuric chloride react, a white precipitate of mercurous chloride is obtained and stannic chloride is formed in solution. Here mercuric chloride is reduced to mercurous chloride, and at the same time stannous chloride is oxidised to stannic chloride,

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

With excess of stannous chloride grey metallic mercury results as a precipitate from the reduction of mercurous chloride stannic chloride being formed in solution simultaneously :—

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

(*c*) A chemical change is one in which the specific properties, physical as also chemical, of a substance undergoing such change are altered completely. In a chemical change new substance or substances with entirely different properties are obtained from the substance undergoing such change. For example, sulphur is a substance possessing certain specific properties, *viz.*, it is a yellow solid with specific chemical properties, but when it burns in oxygen, it forms a new substance which is gaseous and colourless and which possesses chemical properties entirely different from those of sulphur. Here, sulphur has undergone a chemical change. Such changes in properties produced are permanent and cannot be easily reversed. Moreover, during such chemical change there is marked evolution of heat. In some cases also absorption of heat takes place. In a chemical change molecules of the original substance are changed into new types of molecules of other substance or substances. Thus in the example cited, molecules of sulphur are changed into molecules of sulphur dioxide, an entirely new substance in respect of sulphur.

A physical change, on the other hand, alters only the physical properties of a substance. No new substance is produced when any material undergoes such physical change. For example, when a platinum wire is held in a Bunsen flame it becomes red-hot and begins to emit red light, the material remains the same, *viz.*, platinum.

But this change is temporary ; as soon as the wire is removed from the flame the characteristic property of emitting red light is lost and original platinum wire is produced. On the other hand, in a physical change there is no marked evolution or absorption of heat. But the only exception is the absorption of latent heat during change of state of aggregation. As for example, water, when cooled, yields ice by absorption of the latent heat of fusion of ice and water, also when heated to its boiling point, is converted into water vapour completely by absorption of latent heat of steam. But whether in the solid state as ice, or in the liquid state as water, or in the vapourous state as steam, the molecules remain the same and the chemical properties are the same. Also, by altering the external conditions only, *viz.*, pressure and temperature, the above changes undergone by water can be reversed.

(*d*) A *catalytic agent* may be defined as a substance which, when present in a comparatively small amount, either increases or diminishes the rate of a chemical reaction without itself undergoing any change in mass and in chemical composition at the end of the reaction.

Thus manganese dioxide, added in small amount to potassium chlorate, enhances the rate of decomposition of potassium chlorate on heating, but at the end of the reaction it is got back in the same amount with the same composition.

Q. 3. *Describe, giving equations, the preparation of hydrogen peroxide. State its uses. What is the action of hydrogen peroxide on (a) lead sulphide ; (b) acidified potassium iodide ; (c) silver oxide ; (d) acidulated potassium permanganate ? Write equations.*

Ans: Finely powdered commercial barium peroxide is made into a paste with water and this paste is gradually added to dilute sulphuric acid taken in a beaker placed in crushed ice in a trough for cooling its contents. The mixture is stirred with a glass rod and the addition of the paste of barium peroxide is continued until the solution is just faintly acidic.

Barium peroxide reacts with sulphuric acid, forming hydrogen peroxide in solution and a white precipitate of barium sulphate. The precipitated barium sulphate is allowed to settle and then filtered off. The filtrate is an aqueous solution of hydrogen peroxide.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

N. B. (*i*) Anhydrous barium peroxide is not acted upon readily by sulphuric acid on account of a coating of insoluble barium sulphate being formed on it.

(*ii*) The reaction is to be carried out in such a way that the reaction mixture is left a bit acidic, because a trace of acid stabilises hydrogen peroxide.

Uses of H_2O_2.—(1) Hydrogen peroxide is used for restoring the colour of old oil-paintings. The colour of old oil-paintings become black due to the change of white lead used in painting into black lead sulphide by atmospheric sulphuretted hydrogen. Washing with H_2O_2 changes the black PbS into white $PbSO_4$. (2) It is used for bleaching delicate materials like wool, silk, feather, ivory, etc. (3) Mixed with a little nitric acid, it is used as an auricome for colouring hair golden-yellow. (4) It is employed as an antiseptic wash in surgery in dressing spurratic wounds. It is also used largely as a gargle and mouth-wash. (5) Oftentimes it is used as an *antichlor* for removing excess of chlorine from fabrics bleached with that material :—$H_2O_2 + Cl_2 = 2HCl + O_2$. (6) In the laboratory it is used as an oxidising agent.

(*a*) Hydrogen peroxide reacts with lead sulphide, producing lead sulphate by oxidation of PbS, itself being reduced to water.

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

(*b*) Hydrogen peroxide reacts with acidified potassium iodide, liberating iodine by oxidation and is itself reduced to water.

$$2KI + H_2O_2 + 2HCl = 2KCl + I_2 + 2H_2O.$$

(*c*) Hydrogen peroxide reacts with silver oxide producing metallic silver by reduction ; oxygen is evolved as gas and water is formed during such reaction.

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

(*d*) Hydrogen peroxide reacts with acidulated potassium permanganate with mutual reduction. The pink colour of permanganate is discharged, due to the formation of a manganous salt and brisk evolution of oxygen takes place.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Q. 3. *Alternative :*

How is sulphuretted hydrogen prepared in the laboratory ? Give a sketch of the apparatus used.

How would you prove that hydrogen sulphide contains its own volume of hydrogen ?

Ans. Sulphuretted hydrogen is most conveniently prepared in the laboratory by the action of cold, dil. HCl or H_2SO_4 upon ferrous sulphide. For small quantities, a Woulfe's bottle is used and for comparatively large quantities, Kipp's apparatus is employed.

The ferrous sulphide, FeS, in broken fragments, is introduced into the central globe of the Kipp's apparatus. The stop-cock is opened and dil. H_2SO_4 is poured down the safety funnel at the top till the liquid fills the lowest globe and then rises into the central globe. Here the acid comes in contact with FeS : sulphuretted hydrogen is produced and escapes through the stop-cock. The gas is collected by upward displacement of air.

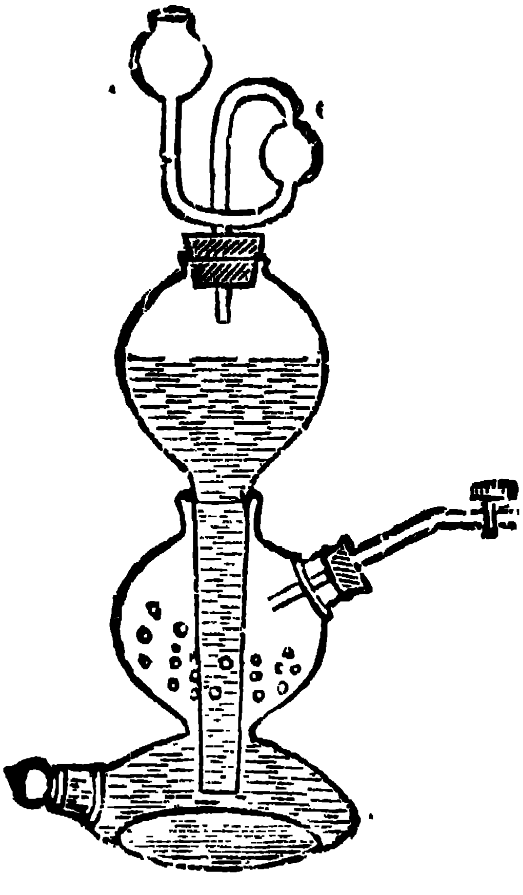


Fig. 96

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

When the gas is not required, the stop-cock is closed ; the gas collects in the central globe, and the pressure of the gas forces the acid out of the central globe. The acid rises up the stem and goes to the topmost globe. Thus further reaction stops. When the gas is required, the stop-cock is opend, H_2S escapes, the acid comes down from the topmost globe and so the contact between FeS and H_2SO_4 is brought about. Hence fresh quantities of H_2S are evolved.

That sulphuretted hydrogen contains its own volume of hydrogen can be proved in the following way :—

A thumb-tube is completely filled with mercury and inverted over mercury in a trough. A few c.c. of dry sulphuretted hydrogen is collected in the tube by displacement of mercury. The volume is carefully marked by means of a rubber ring after adjusting the mercury level to the same position inside and outside the tube, A piece of metallic tin is introduced into the horizontal part of the tube. and it is heated by a burner from outside. Tin combines with sulphur of sulphuretted hydrogen forming tin sulphide and liberating hydrogen. After allowing the tube to cool to the ordinary temperature, the mercury level is adjusted and found to stand at the same level as before. The residual gas is proved to be hydrogen by the facts that it burns with a scarcely visible blue flame with the production of water only and is absorbed by metallic palladium. Hence, the volume of hydrogen liberated is equal to the volume of sulphuretted hydrogen decomposed, or sulphuretted hydrogen contains its own volume of hydrogen.

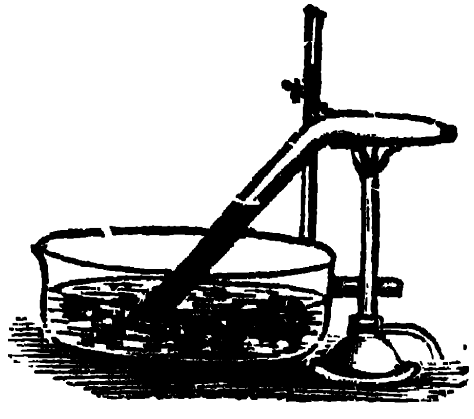


Fig. 97

Q. 4. *Give an account of the manufacture of sodium carbonate by the ammonia-soda process, and explain the reactions which occur.*

How is sodium carbonate converted into caustic soda? Give the chief uses of the latter both in the laboratory and on a large scale.

Ans. The modern method for the manufacture of sodium carbonate from common salt is the ammonia-soda process or Solvay process. This is based on the reaction between sodium chloride solution and ammonium bicarbonate solution, produced by saturating ammoniated brine with carbon dioxide, with the precipitation of sodium bicarbonate :—

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$
$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

The precipitated sodium bicarbonate is filtered and then heated to yield sodium carbonate :—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The working of the process will be clear by referring to the adjoining diagram, which gives a sketch of the plant used in the operation of the process.

The working of the process is as follows :—

(*a*) A strong solution of sodium chloride (brine) is obtained directly from salt-beds by pumping in water into the salt-beds and then pumping out the brine so produced into a brine reservoir (shown on the top left). Brine from that reservoir is next admitted into the saturating tank, which is an upright cylinder. Here the brine is saturated with ammonia. The salts of calcium and magnesium contained in the brine are precipitated by carbon dioxide, coming along with ammonia from the ammonia recovery plant :—

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$
$$CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + CaCO_3$$
$$MgCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + MgCO_3.$$

The brine, when fully saturated with ammonia, is run into a settling tank, where the precipitated calcium and magnesium carbonates settle down.

(*b*) Ammoniated brine is then pumped up from the settling tank to the top of the carbonating tower, provided with perforated horizontal partitions and cooling coils and is made to trickle down the tower. Carbon dioxide gas is admitted at the bottom of the tower, so that carbonation is carried out on the principle of counter currents. Carbon dioxide rises in small bubbles through the perforations. The ammonium bicarbonate formed by the interaction of carbon dioxide, ammonia and water, reacts with sodium chloride solution, precipitating sodium bicarbonate :—

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$
$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

The milky liquid containing small crystals of sodium bicarbo-

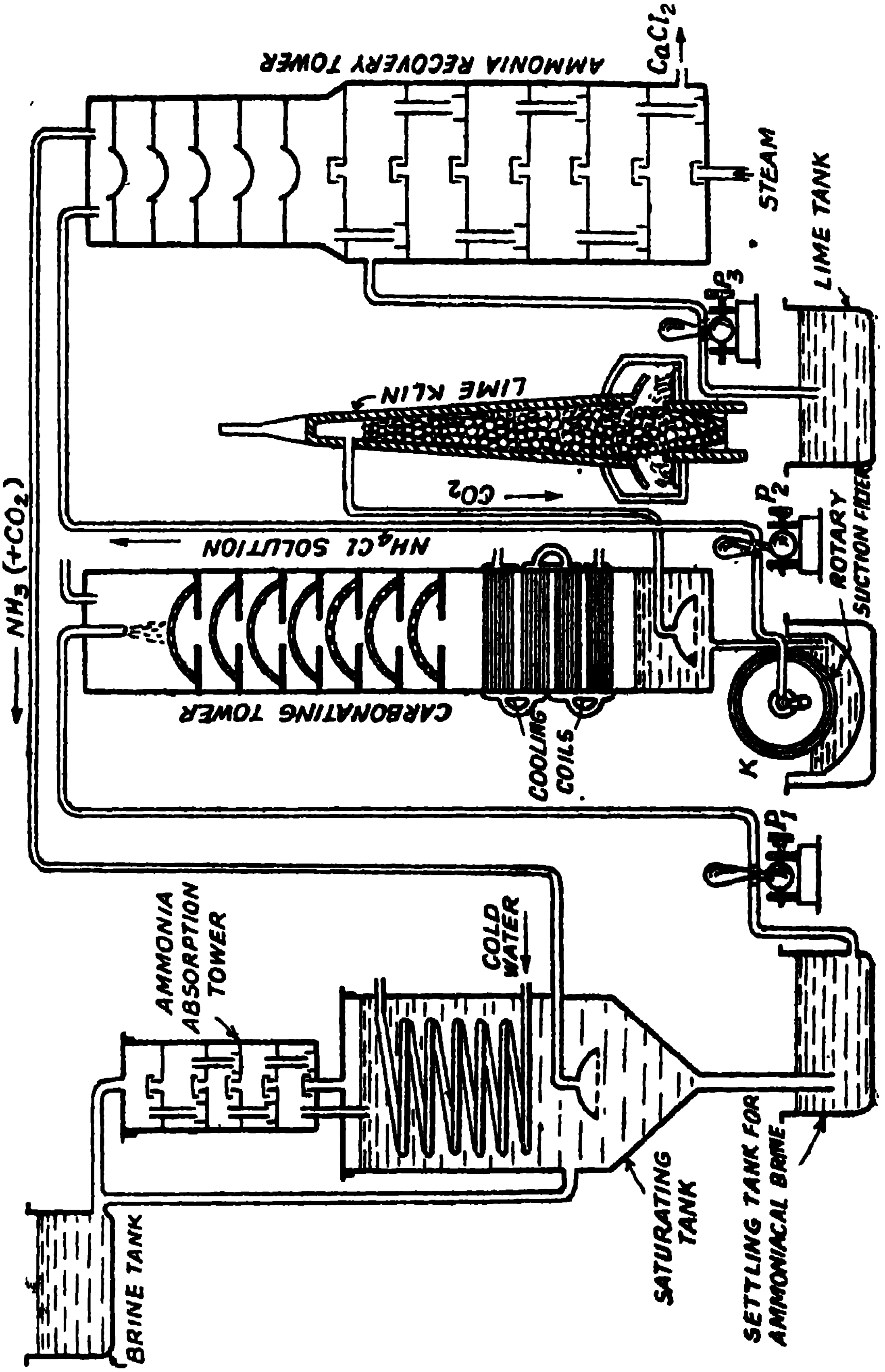


Fig. 98

nate is drawn off at the base of tower and filtered at the rotary vacuum filter. The crystals of sodium bicarbonate are deposited as a layer on the outside of the filter and are collected by scraping with a knife-blade. The mother liquor containing ammonium chloride and some ammonium bicarbonate is pumped to the top of the ammonia-recovery tower.

The sodium bicarbonate is next calcined in a covered pan or a rotary furnace fired on the outside. Sodium carbonate is formed and carbon dioxide and steam escape as gas :—

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide evolved here is utilised in the carbonating tower together with the gas from the lime-kiln.

(*c*) In lime-kiln limestone is heated strongly to give carbon dioxide and calcium oxide (quicklime) :—

$$CaCO_3 = CaO + CO_2.$$

The carbon dioxide is led to the carbonating tower, while the quicklime is slaked with a large quantity of water and pumped on to the ammonia recovery plant in the form of milk of lime.

(*d*) In the ammonia-recovery tower, which consists of an upper and a lower part, the mother liquor is fed into the top of the upper part and at the top of the lower part milk of lime is admitted. A current of steam is next admitted at the base of the tower. Ammonium bicarbonate is decomposed by steam, and ammonium chloride is decomposed by lime :—

$$NH_4HCO_3 = NH_3 + H_2O + CO_2$$
$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

The mixture of ammonia with the small amount of carbon dioxide passes on to the saturating tank.

Thus the process is self-sufficient, but certain amount (about 2%) of ammonia is lost during working and is to be replaced.

Conversion of sodium carbonate into caustic soda :—Sodium carbonate in water solution is run into *causticisers*, i.e., iron tanks provided with mechanical agitators and fitted with a pipe for admission of steam. Quicklime placed in an iron cage is kept dipping into the top of the solution, the stirrer is worked and steam is passed in. Sodium carbonate then reacts with calcium hydroxide formed from CaO and is practically completely converted into caustic soda.

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3 \quad \text{(pptd')}$$

The precipitated calcium carbonate is filtered off and caustic soda solution so obtained is evaporated in iron pans to get solid caustic soda.

In the laboratory caustic soda is employed both in qualitative and in quantitative analysis. In qualitative analysis, separation of iron from aluminium is carried out with its help and in quantitative analysis, it is used as a strong alkali in acidimetry and alkalimetry.

Q. 4. *Alternative* :

How is bromine obtained commercially ? In what form does it commonly occur in nature ? Compare **three** *physical properties of chlorine and bromine, and outline* **two** *sets of experiments you would perform to compare the chemical properties of these two elements.*

Ans. In American practice bromine is at present obtained commercially from sea-water. Sea-water is drawn at a point near the chemical works and allowed to settle in an artificially prepared tank. After removal of the suspended matter, sea-water is first acidified and then chlorinated. Bromine is liberated and renders the water slightly yellow in colour. The liberated bromine is blown out with a current of air and, is absorbed in Na_2CO_3 solution. The solution is afterwards treated with excess of an acid, and bromine which is set free is distilled off in steam.

$$3Br_2 + 3Na_2CO_3 = 5NaBr + NaBrO_3 + 3CO_2$$

$$NaBrO_3 + 5NaBr + 3H_2SO_4 = 3Br_2 + 3Na_2SO_4 + 3H_2O.$$

It is purified by first distilling it with potassium bromide (for removing chlorine) and then distilling the product with conc. H_2SO_4 (for removing water).

Bromine occurs in nature as magnesium bromide, both in carnallite KCl, $MgCl_2$, $6H_2O$, found at Stassfurt in Germany, in which bromocarnallite, KBr, $MgBr_2$, $6H_2O$, occurs as an impurity as also in sea-water. It is also met with as bromides of sodium, potassium and calcium, in mineral water and in certain salt deposits. Silver bromide, AgBr, is also sometimes found in nature.

Comparison of **three** *physical properties of chlorine and bromine* :—

Chlorine	Bromine
1. Chlorine is a gas.	1. Bromine is a liquid.
2. Its colour is greenish-yellow.	2. Its colour is dark-red.
3. Specific gravity of liquid chlorine is 1·55.	3. Specific gravity of bromine is 3·19.

Expt. 1. Chlorine taken in a gas-jar is mixed with hydrogen in the dark and the mixture exposed to direct sun-light, when explosion occurs with the formation of hydrogen chloride.

$$H_2 + Cl_2 = 2HCl.$$

Bromine vapour is similarly mixed with hydrogen in a gas-jar in the dark and the mixture exposed to direct sun-light. No explosion occurs and no combination between bromine and hydrogen taken place under this condition.

This shows that the affinity of bromine for hydrogen is less than that of chlorine.

Expt. 2. Starch solution is taken in the beaker and to that a solution of chlorine in water is added. No change in colour takes place. But when a solution of bromine in water is added to starch solution taken in a beaker, strach solution is coloured yellow.

Thus chlorine has no action on starch solution, but bromine produces a yellow colouration with it.

Q. 5. *Give an account of the manufacture and purification of coal gas, and mention the nature and importance of any* **two** *by-products obtained in the process.*

Ans. Bituminous or soft coal is heated in D-shaped fire-clay retorts in furnaces which are fired with producer gas to a temperature of 1000°C. The volatile products given off pass up the exit pipes called *ascension pipes*, fitted over the retorts. These pipes at the other end are in communication with the *hydraulic main* where the gas is partially cooled and some tar and water condense. From the hydraulic main the hot gases pass into a series of iron pipes, called *condensers*. Here the gases are cooled, and more tar is condensed and run into *tar-well*. The liquid in the tar-well separates into two layers—the upper layer is mainly a solution of ammonia and ammonium salts in water and is called *gas-liquor* or *ammoniacal liquor* ; the lower layer is called *gas-tar* or *coal-tar*. Next the gases are drawn out of the condensers by means of *pumps* and are forced up a tower filled with coke—called *scrubber*—down which cold water trickles. All traces of ammonia are removed in this way. The gases are next passed through a *purifier* which is an iron tank containing slaked lime, $Ca(OH)_2$, in which CO_2, H_2S and other sulphur compounds are absorbed.

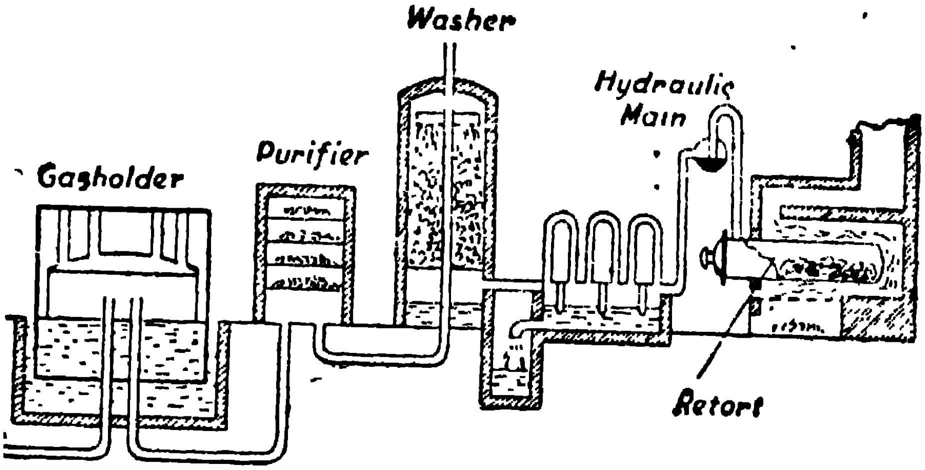


Fig. 99

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O.$$

A further purification is effected by passing the gases through another purifier containing hydrated oxide of iron which takes up the last traces of H_2S and cyanogen :—

$$2Fe\,(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

Thus purified coal gas is stored over water in big gas-holders.

There are several by-products of coal-gas industry. One of these is ammoniacal liquor, which contains ammonia and ammo-

nium salts dissolved in water. It is utilised to get liquor ammonia of commerce as also ammonium sulphate which is used as a fertiliser. Another by-product to be mentioned is gas-carbon. It is obtained as a dense deposit in the upper cooler part of the retort. It is sublimed carbon. It is employed in the electric cells and also as carbon-pencils in arc-lamps.

SECOND PAPER

Q. 1. *Explain the terms : (a) Ion, (b) Electro-chemical equivalent, (c) Faraday.*

Two cells, one containing copper sulphate and the other silver nitrate were placed in the same electric circuit. It was found that 0'106 gm. of copper was deposited in the same time as 0'3597 gm. of silver. Calculate the equivalent of silver and also find out the amount of silver which will be deposited when a current of 1'05 ampères is passed through the solution of silver nitrate for 20 minutes.

Given chemical equivalent of copper = 31'8.

Ans. (*a*) An ion is an electrically charged atom of an element or a compound radical, usually formed during the reversible electrolytic dissociation of an acid, base or salt in aqueous solution or in the fused state. The metallic part present in a salt or hydrogen present in an acid gives rise to a positively-charged ion under the circumstances mentioned and is known as *cation* and the acidic part gives rise to a negatively-charged ion, and is called *anion*. Thus, when NaCl is put into aqueous solution, both cation Na^+ and anion Cl^- are produced therein. Even in fused state such ions are formed from NaCl. Both cation and anion are produced in equal amounts and so the solution remains electrically neutral. The term 'ion' means electricity-carrier and during electrolysis, *cation* travels with the electric current and is deposited at the cathode and *anion* travels in opposite direction and is deposited at the anode. Another example is aqueous solution of sulphuric acid, which contains H^+-ion (cation) and $SO_4^=$ (anion).

(*b*) The mass in grams of an element which is liberated by the passage of unit quantity of electricity, *viz.*, 1 coulomb (*i. e.*, 1 ampere of current flowing for 1 second through the solution containing the element in combination), is called the Electrochemical Equivalent of the element.

Thus, by passing 1 ampere of electric current for 1 second through a dilute solution of sulphuric acid, 0·0000104 gm. of hydrogen is liberated at the cathode. Hence the electro-chemical equivalent of hydrogen is 0·0000104 gm.

(*c*) Faraday is an unit in measuring the quantity of electricity. It is that quantity of electricity which can liberate during electrolysis one gram-equivalent of any element or radical. It is equal to about 96,500 coulombs of electricity, where 1 coulomb indicates the quantity of electricity obtainable when 1 ampere of current flows for 1 second.

From Faraday's second law of electrolysis, we have,

$$\frac{\text{Mass of copper liberated}}{\text{Mass of silver liberated}}=\frac{\text{chemical equivalent of copper}}{\text{chemical equivalent of silver}}$$

Hence, $\dfrac{0{\cdot}106}{0{\cdot}3597}=\dfrac{31{\cdot}8}{\text{Chemical equivalent of silver}}$

Therefore, chemical equivalent of silver

$$=\frac{31{\cdot}8\times 0{\cdot}3597}{0{\cdot}106}=107{\cdot}91.$$

Also, the amount of silver deposited under the given conditions $=0{\cdot}001118\times 1{\cdot}05\times 20\times 60$ gm.

(where 0·001118 is the electro-chemical equivalent of silver) $=1{\cdot}40868$ gm.

Q. 1. *Alternative* :

Explain the following terms :—normal, acid, and basic salts. Give examples of each.

1·08 gm. of ammonium chloride was boiled with 62 c. c. of $\frac{N}{2}$ *NaOH till free from ammonia, 44 c. c. of* $\frac{N}{4}$ *HCl were required for neutralising the excess of alkali in the mixture. Calculate the percentage of ammonia in the salt.*

$(Na=23{\cdot}0,\ O=16{\cdot}0,\ N=14{\cdot}0)$.

Ans. A salt is a compound produced by the partial or complete replacement of the replaceable hydrogen atom or atoms present in the molecule of an acid by a metal or a group of elements behaving like a metal. Thus, NaCl is a salt of hydrochloric acid, HCl, in which the metal Na has replaced the replaceable hydrogen atom of hydrochloric acid.

Salts have been classified as normal salts, acid salts and basic salts.

A salt, produced by the replacement of all the replaceable hydrogen atoms of an acid by a metal or a group of elements behaving like a metal (*e.g.*, NH_4), is called a *normal salt.* Thus, NaCl, $(NH_4)_2SO_4$, Na_3PO_4 are normal salts of HCl, H_2SO_4, and H_3PO_4 respectively.

A salt, produced by the partial replacement of the replaceable hydrogen atoms of a dibasic or tribasic (or generally polybasic) acid by a metal or a group of elements behaving like a metal, is called an *acid salt.* Thus, $KHSO_4$, $NaHCO_3$, NaH_2PO_4, are acid salts of H_2SO_4, H_2CO_3 and H_3PO_4 respectively.

A *basic salt* is one formed by the partial replacement of the replaceable hydroxyl groups of a di-acid or tri-acid (or generally poly-acid) base, by the acid group of an acid. Thus, $Pb(OH)NO_3$ is basic lead nitrate.

It is also defined as the salt produced by the union of a larger proportion of a base than is necessary for the normal salt. For example, basic lead carbonate $2PbCO_3$, $Pb(OH)_2$ (white lead) is a basic salt.

$$62 \text{ c.c. of } \frac{N}{2} \text{ NaOH solution} \equiv 62 \times \tfrac{1}{2} \text{ c.c. of (N)NaOH sol.}$$

$$\equiv 31 \text{ c.c. of (N)NaOH sol.}$$

$$44 \text{ c.c. of } \frac{N}{4} \text{ HCl solution} \equiv 44 \times \tfrac{1}{4} \text{ c.c. of (N)HCl sol.}$$

$$\equiv 11 \text{ c.c. of (N)HCl sol.}$$

$$\equiv 11 \text{ c.c. of (N)NaOH sol.}$$

Therefore, 11 c.c. of (N)NaOH solution was left over from 31 c.c. of (N)NaOH solution added after driving off all the ammonia.

Hence, for removing all the ammonia from the ammonium chloride supplied, the amount of (N) NaOH sol. required = (31 − 11) c.c. = 20 c.c.

Now, from the equation,

$$\underset{40}{NH_4Cl + NaOH} = NaCl + H_2O + \underset{17}{NH_3}$$

We know that 40 grams of caustic soda displace 17 grams of ammonia. But 40 grams of NaOH are present in 1000 c.c. of (N) NaOH solution.

Therefore, 1000 c.c. (N) NaOH sol. ≡ 17 gm. of NH_3
Hence, 1 c.c. „ ≡ 0·017 gm. „
Therefore, 20 c.c. „ ≡ 0·017 × 20 gm.
≡ 0·34 gm.

Thus, 1·08 gm. of ammonium chloride supplied contains 0·34 gm. of NH_3.
∴ 1 gm. „ „ „

contains $\frac{0·34}{1·08}$ gm. of NH_3.

Therefore, ammonia present in ammonium chloride supplied $= \frac{0·34}{1·08} \times 100\% = 31·48\%$.

Q. 2. *Give a brief account of the periodic classification of elements. Show that the chemical properties of magnesium and zinc justify their position in the same group of the periodic table.*

Ans. In 1869 the Russian Chemist Mendeleeff and in 1870 the German Chemist Lothar Meyer, discovered, quite independently of each other, that by arranging the elements in the order of their increasing atomic weights, their properties were found to vary from member to member in a definite manner, but these were found to return more or less to the same value at fixed points in the series.

Mendeleff arranged the elements in a table in the order of their increasing atomic weights in a horizontal series, making it a point that elements having similar properties were placed in the same vertical column. In making that arrangment Mendeleff had to leave many blank spaces in the table and at least in two cases he had to break the atomic weight sequence. He called the horizontal rows *Periods* and the vertical columns *Groups*. He again subdivided each group into two sub-groups, A and B.

Original arrangement of Mendeleff has now undergone many changes due to discovery of new elements since then. The Periodic Table as it stands now consists of nine vertical columns or groups, headed by the Roman numbers from O to VIII. The periods are called short or long according to the number of elements contained in them. The first period consists of two elements, Hydrogen and Helium. The second period contains 8 elements, starting from Lithium and ending in Neon. This is known as *first short period*. The third period contains also 8 elements starting from Sodium and ending in Argon. This is called second short period. The next period consists of 18 elements, starting from Potassium and ending in Krypton. It is known as the *first long period*. Similarly we have also a *second long period*, containing 18 elements also, starting from Rubidium and ending in Xenon. Next period is a *very long period*, containing 32 elements in which all the fifteen rare-earth elements are included, and it starts from Caesium and ends in Radon. Then comes a fragmentary period containing only six radioactive elements.

Now according to Groups, zero group comprises all the inert gases of the atmosphere. Sub-group A of Group I contains the alkali metals and sub-group B of Group I consists of the coinage metals : Copper, silver, gold. Elements of the same sub-group are chemically similar.

This periodic arrangement of elements has helped enormously in systematising the study of Inorganic chemistry. It has rendered the study of nearly 90 diverse elements into a study of only 9 vertical columns. It has also helped in the correction of doubtful atomic weights. This arrangement has also given impetus to research.

There are certain similarities in chemical properties of magnesium and zinc. These are :—

(1) Both these elements burn in oxygen, forming their respective oxides.

(2) Heated magnesium decomposes steam :—$Mg + H_2O = MgO + H_2$.

Zinc decomposes boiling water : $Zn + H_2O = ZnO + H_2$.

(3) The Salts of magnesium and zinc are crystalline and hydrated : *e.g.*, $MgCl_2, 6H_2O$, $ZnCl_2, H_2O$

$MgSO_4, 7H_2O$, $ZnSO_4, 7H_2O$

$Mg(NO_3)_2, 6H_2O$, $Zn(NO_3)_2, 6H_2O$.

The chlorides decompose, due to hydrolysis, on heating. The sulphates are isomorphous and soluble in water.

(4) Valency of both magnesium and zinc is 2 in all their compounds, thus justifying their inclusion in Group II of the Periodic Classification.

But, it must be remembered that magnesium is a *typical* element of Group II, whereas zinc belongs to sub-group B of Group II.

Q. 3. *How would you establish the volumetric composition of ammonia ? Explain with equations the action of ammonia gas on (a) heated sodium, (b) red-hot black copper oxide, (c) oxygen when mixed and ignited. In what respects ammonia resembles phosphine ?*

Ans. The volumetric composition of ammonia can be determined by Berthollet's Eudiometric method. A known volume (say 10 c.c.) of *pure* and *dry* Ammonia gas is collected in a graduated eudiometer tube over mercury, the reading of the volume being taken after adjusting the mercury level to the same height inside and outside the tube. There are two Pt-wires sealed near the closed end of the tube and with their help a series of electric sparks are passed, by connecting them to the terminals of an induction coil, through the ammonia gas, when Ammonia is decomposed into Nitrogen and Hydrogen and the volume of the gas goes on increasing. The sparking is stopped when no further increase in volume is observed. Mercury level is again adjusted and the volume of the mixture of N_2 and H_2 is read off. It is found to be 20 c.c. Next an excess of oxygen is added, the mercury level is adjusted and the volume of the mixture with oxygen is noted. The mixture is then exploded by passing a single electric spark through the mixture from an induction coil. Hydrogen and Oxygen combine to form steam which condenses into liquid water. The apparatus is cooled, the mercury level is again adjusted and the reading of the volume noted.

The following are the readings obtained :—

Vol. of Ammonia taken = 10 c.c.
Vol. of $N_2 + H_2$ after sparking = 20 c.c.
Vol. after addition of oxygen = 30 c.c.
Vol. of the residual gas (N_2 + excess of O_2) after explosion = 7·5 c.c.
∴ Contraction after explosion = (30 − 7·5) c.c. = 22·5 c.c.

This contraction is due to the formation of water ; two-thirds of the contraction is equal to the volume of Hydrogen present, since two volumes of Hydrogen combine with one volume of Oxygen to form water which occupies zero volume. Hence volume of Hydrogen = $\frac{2}{3} \times 22{\cdot}5$ or 15 c.c, and vol. of Nitrogen = (20 − 15) or 5 c.c. Thus, 10 c.c. of Ammonia yield on decomposition 15 c.c. of Hydrogen and 5 c.c. of Nitrogen.

That is to say, 1 vol. of Nitrogen combines with 3 vol. of Hydrogen to give rise to 2 vols. of Ammonia.

By applying Avogadro's hypothesis, it can be shown that 1 mol. of N_2 combining with 3 mols. of H_2 give rise to 2 mols. of Ammonia. Therefore 1 mol. of Ammonia contains 1 atom of Nitrogen and 3 atoms of Hydrogen. So the formula for Ammonia is NH_3. This is confirmed by the experimental determination of its gaseous density which is found to be 8·5, thus tallying with half the molecular weight.

(*a*) When ammonia is passed over heated sodium, hydrogen gas is liberated and sodamide is formed :—

$$2NH_3 + 2Na = 2NaNH_2 + H_2.$$

(*b*) When ammonia is passed over red-hot black copper oxide, oxidation of ammonia occurs, nitrogen is set free as gas, metallic copper is produced and water is formed as steam, which can be condensed by cooling :—

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2.$$

(*c*) When ammonia is mixed with oxygen and ignited, it burns with a yellowish flame, with the production of water and liberation of nitrogen as gas :—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

Ammonia resembles phosphine (*i*) in formula, *e.g.*, NH_3 and PH_3 ; (*ii*) in basic character, but ammonia is a stronger base with respect to phosphine and combines with all acids to form ammonium salts, whereas phosphine is a weak base and combines only with halogen acids to form phosphonium halides ; *e.g.*

$$2NH_3 + H_2SO_4 = (NH_4)_2\ SO_4, \text{ but } PH_3 + HI = PH_4I.$$

(*iii*) in their reactivity towards chlorine :—

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$$
$$PH_3 + 4Cl_2 = 3HCl + PCl_5.$$

(*iv*) in the action of heat on them, dissociation into elements occurring in both cases :

$$2NH_3 = N_2 + 3H_2\ ;\ 2PH_3 = 2P + 3H_2.$$

Q. 4. *Describe and explain the changes which take place when (a) sulphuretted hydrogen is passed into a solution of ferric chloride, (b) aluminium powder is boiled with concentrated caustic soda solution, (c) sodium carbonate is added to a solution of aluminium chloride, (d) nitric acid is added to a solution of ferrous sulphate, (e) monosodium hydrogen phosphate is heated. Give equations.*

Ans. (*a*) The yellow solution of ferric chloride turns colourless and at the same time it turns turbid. The discharge of colour is due to reduction of ferric chloride to ferrous chloride by sulphuretted hydrogen and the turbidity is due to separation of sulphur. The solution also contains hydrochloric acid formed during the reaction.

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

(b) When aluminium powder is boiled with concentrated caustic soda solution, aluminium passes into solution as sodium aluminate. Water also takes part in the reaction. Hydrogen gas is evolved. This is due to the amphoteric nature of the metal and its oxide.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

(*c*) Thick precipitate of aluminium hydroxide is formed, due to hydrolysis of the solution. No carbonate is formed of aluminium, on account of the weak basic character of the metal. Carbon dioxide is evolved as gas. Water of the solution takes part in the reaction.

$$2AlCl_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3CO_2.$$

(*d*) When nitric acid is added to a solution of ferrous sulphate which is green in colour, the colour of the solution becomes brown. This is due to oxidation of ferrous sulphate to ferric sulphate, nitric acid being reduced to nitric oxide, which dissolves in any remaining ferrous sulphate which has escaped oxidation producing a brown solution containing a loose compound of $FeSO_4$ and NO, *viz.*, $FeSO_4$, NO. The reaction takes place readily in presence of conc. H_2SO_4, but even in its absence the oxidation takes place though not completely.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO = FeSO_4, NO.$$

This reaction is the basis of *ring test* for nitric acid and nitrates.

(e) On heating monosodium hydrogen phosphate, the mass swells up, water is lost as steam and a residue of sodium metaphosphate is left behind.

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Q. 5. *Describe the preparation and uses of the following substances* : (*a*) *Water-glass*, (*b*) *Green vitriol*, (*c*) ***Red lead***, (*d*) *Lunar caustic*, (*e*) *Stannic chloride.*

Ans. (*a*) Water-glass is water-soluble glass and is either water-soluble soda glass, Na_2SiO_3 or water-soluble potash glass (K_2SiO_3). It is prepared by fusing together a mixture of either sodium or potassium carbonate, finely powdered white sand and charcoal in a small reverberatory furnace. An aqueous solution of soluble soda or potash glass is known as water-glass.

Water-glass is used as a filler in cheap soaps, for fire-proofing textiles and timbers, as a mordant in textile-dyeing and printing, for preserving eggs and as a cement for certain purposes.

(*b*) Green vitriol is ferrous sulphate hepta-hydrate, $FeSO_4$, $7H_2O$. Pianowire, which is made of wrought iron, is dissolved in chemically pure sulphuric acid diluted with water. The solution so obtained is filtered and evaporated in absence of air, when green crystals of $FeSO_4$, $7H_2O$ will separate out.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Green vitriol is usually obtained as a by-product in the laboratory from Kipp's apparatus for generating sulphuretted hydrogen for analytical purposes where ferrous sulphide is reacted upon by dil. sulphuric acid.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The waste liquid collected at the bottom of the Kipp's apparatus is taken out, filtered, and evaporated to crystallisation when pale-green crystals of hydrated ferrous sulphate, or green vitriol separates out.

Ferrous sulphate is used in the preparation of writing ink; in the manufacture of jeweller's rouge, in dyeing industry and in medicine.

(c) Red lead is also known as *minimum* and is triplumbic tetroxide, Pb_3O_4. It is usually prepared from lead. Lead is heated in a current of air, whereby it is converted into lead monoxide, PbO. Lead monoxide is removed and ground, whereby any particle of unoxidised lead is flattened out and then easily removed by means of sieves. Finely powdered lead monoxide is next heated either in a reverberatory furnace or in a barrel-shaped vessel, open at both ends, in excess of air at 400°C. for two consecutive days. The temperature should not be allowed to go above 400°C. for in that case red lead formed will decompose. The material is taken out, cooled, washed, dried and sent out to the market

$$6Pb + 3O_2 = 6PbO$$
$$6PbO + O_2 = 2Pb_3O_4.$$

Red lead is used as a paint; in the manufacture of flint glass and in the manufacture of matches; as an oxidising agent in the laboratory.

(d) Lunar caustic is silver nitrate, $AgNO_3$. It can be prepared by dissolving pure metallic silver in moderately dilute nitric acid, filtering the solution so obtained and then evaporating the filtered solution to crystallisation when colourless tabular crystals separate. These are separated from solution by filtration and washing with a little water.

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O.$$

Silver nitrate is used in medicine as cauterising agent, in photography for impregnating gelatin with photohalides, in silvering of mirrors, in the preparation of marking ink, and as a reagent in chemical analysis in the laboratory, both qualitative and quantitative.

(*e*) Stannic chloride, $SnCl_4$, is prepared by passing dry chlorine over molten tin placed in a distilling flask which is connected to a receiver kept cool, $Sn + 2Cl_2 = SnCl_4$. Stannic chloride collects in the receiver as a fuming liquid.

It can also be obtained by distilling a mixture of powdered tin with an excess of mercuric chloride.

$$Sn + 2HgCl_2 = 2Hg + SnCl_4.$$

$SnCl_4$ distils over and collects in a cooled receiver as a fuming liquid.

Stannic chloride, in the hydrated form $SnCl_4, 5H_2O$, is used under the name "butter of tin" as a mordant in dyeing and calico-printing. *Pink salt* is a double chloride. $(NH_4)_2SnCl_6$, and is also used similarly.

Q. 6. *Name the important ores with their formulae from which the following metals are obtained : lead, tin and zinc. Give a brief account of the method by which any* one *of them is produced from its ores, Explain the chemical reactions involved in its extraction. State the uses of the metal and two of its important alloys.*

Ans. Important ores of **lead** are : (1) **Galena**, PbS : (2) **Anglesite**, $PbSO_4$; (3) **Cerussite**, $PbCO_3$; (4) **Pyromorphite**, $3Pb_3(PO_4)_2, PbCl_2$.

Important ore of **tin** is only one, viz., **Cassiterite** or **tinstone**, SnO_2.

Important ores of **zinc** are : (1) **Zinc blende**, ZnS ; (2) **Calamine** or **Smithsonite**, $ZnCO_3$ and (3) **Red Zinc ore** or **Zincite**, ZnO.

Extraction of Lead :—Lead is now-a-days extracted by a blast-furnace operation from galena, PbS. The ore is first crushed into fine powder and the powdered ore is mixed with pine oil and water. A blast of air is then blown through the mixture when a large quantity of froth is produced, which takes up along with it the particles of galena. The worthless impurities like silica etc. sink down. The froth is skimmed off and collected.

The concentrated ore is next sintered in a pot, mounted on trunnions and provided with a hood for collecting fumes. The ore, after drying, is mixed with coke and lime stone and fed into the pot which has a fire on a grating beneath. A slow blast of air is passed through the bottom. Sulphur present in galena burns out to SO_2 which escapes as gas and lead oxide is produced. The ore is by this means agglomerated into a porous cake.

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$
$$PbS + 2O_2 = PbSO_4.$$

A little lead sulphate is also formed.

The sintered mass is broken up into lumps of proper size and fed into a small blast furnace of the water-jacketed type, together with coke, limestone and iron ore through a charging pipe in such a way that the charge settles just beneath the waste-gas outlet. A blast of air is admitted through tuyeres. At first PbO is reduced by carbon present in the charge $PbO + C = Pb + CO$.

The carbon monoxide formed then reduces PbO to metallic lead : $PbO + CO = Pb + CO_2$. Any unchanged lead sulphide reacts with lead oxide and lead sulphate producing metallic lead :

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

The iron ore added reacts with unchanged lead sulphide producing metallic lead and ferrous sulphide :

$$2PbS + Fe_2O_3 + 3C = 2Pb + 2FeS + 3CO.$$

The iron sulphide so formed passes into the slag, which consists of calcium silicate and ferrous silicate formed in the following way :—

$$CaCO_3 = CaO + CO_2$$
$$CaO + SiO_2 = CaSiO_3$$
$$Fe_2O_3 + CO = 2FeO + CO_2$$
$$FeO + SiO_2 = FeSiO_3.$$

The molten slag and the molten lead are drawn off through separate tapping holes provided at the bottom of the furnace.

Extraction of Tin :—

The extraction of tin from tinstone is carried out in four operations :—

(*i*) *Calcination* :— The crushed ore is first washed with water for removing earthy impurities. Tinstone, being heavier than siliceous impurities, settle at the bottom of the washing vessel. The washed ore is next calcined in a revolving calciner. The ore is fed in at the top, hot gases are admitted from a furnace beneath through the bottom, so that as the charge descends, it meets the hot gases travelling upwards. Sulphur and arsenic are converted into SO_2 and As_4O_6 respectively and volatilise away. As_4O_6 .is condensed in flues. Cu and Fe, present in the ore, are converted into their sulphates and oxides.

(*ii*) *Washing* :—The calcined ore is next cooled and washed with water, whereby soluble substances dissolve and the oxide of iron and other light materials are washed away by floatation. Tinstone, being heavy, settles at the bottom of the washing vessel. The ore is now known as **Black-tin** and contains about 60—70% of SnO_2.

When, however, wolfram (ferrous tungstate) is present along with tinstone, it can not be purified by simple washing operation, for wolfram is as heavy as tinstone. During calcination

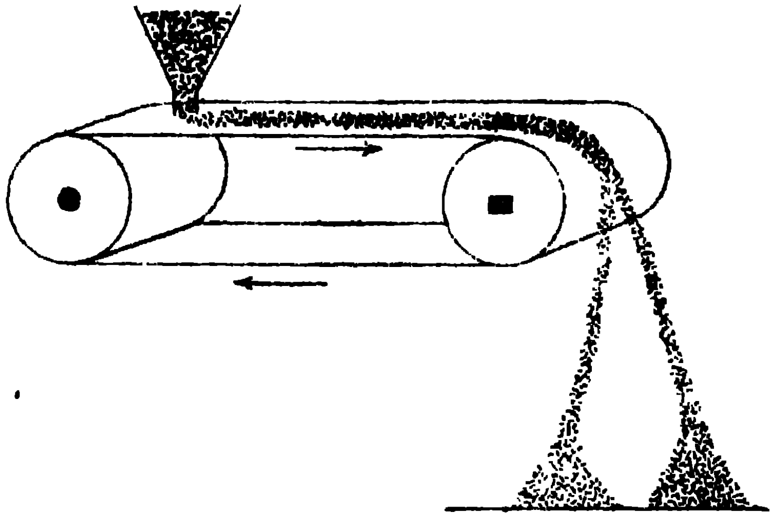


Fig. 100

wolfram is converted into ferric tungstate and so becomes magnetic. Hence a magnetic separation is carried out. The calcined and washed ore is fed on a rotating belt placed on the two poles of a powerful electromagnet. When the mass comes at the end of the belt and falls to the ground, two separate heaps are formed, one of the tinstone freed from wolfram away from the magnet and the other of wolfram near the magnet.

(*iii*) *Reduction or smelting* :—Black-tin is next mixed with anthracite, limestone and sand, and smelted in a reverberatory furnace of a special type, or in a blast furnace. The oxide is reduced to metallic tin, which melts down and collects at the bottom of the furnace and the molten slag collects at its top. The slag is removed and the metal is cast into bars.

$$SnO_2 + 2C = Sn + 2CO.$$

(*iv*) *Refining* :—The metal, thus obtained, is not pure. It is purified by two operations, viz., (1) Liquation and (2) Poling.

(1) Liquation is carried out by melting bars of tin on the sloping hearth of a reverberatory furnace, when the readily fusible tin melts and flows away, leaving the impurities like copper, iron, tungsten, arsenic, etc. behind.

(2) Poling is next carried out in a pot in which liquated tin is fused and the fused metal is stirred with poles of greenwood. Hydrocarbon gases are evolved freely and these, in bubbling out through the molten metal, expose fresh surface of it to the oxidising action of air. Impurities still present in tin, viz, iron, arsenic, etc. are oxidised, which separate out as scum. The scum is removed and commercially pure tin is obtained.

Extraction of zinc :—

Zinc is extracted by the *Carbon Reduction Process.*

In case of zinc blende being used as the ore, it requires to be submitted to a preliminary concentration operation as it contains galena, sand, etc. as impurities. For the purpose the ore is crushed to powder, mixed with pine oil and water with a little acid and the mixture stirred by blowing in air through it. ZnS floats up with the froth formed and is collected by skimming. Impurities settle at the bottom. When calamine is used as ore of zinc, no preliminary concentration is necessary.

The concentrated zinc blende or calamine is next roasted in air, in such a fashion that the sulphide is converted into oxide and not into sulphate. Carbonate is readily converted into oxide by this operation.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnCO_3 = ZnO + CO_2$$

The roasted ore containing ZnO only is next thoroughly mixed with powdered coal (or anthracite) and the mixture is heated to redness in cylindrical retorts made of fireclay in closed furnaces fed by gaseous fuel like producer gas. The retorts are closed at one end, and to the open end of each retort, after charging, a clay tube is luted and this clay tube serves as a condenser for zinc vapour. A large number of such retorts are arranged in such a fashion in the furnace that they are slightly inclined downwards towards the mouth. During heating, ZnO is reduced to metallic zinc and carbon monoxide is evolved as gas. A little excess of coal is used, so that no carbon dioxide may be produced, since CO_2 has an oxidising action on heated zinc.

$$ZnO + C = Zn + CO.$$

Carbon monoxide burns at the mouth of the clay tube with a blue flame. After a while, the flame becomes much more brilliant, and that indicates the volatilisation of zinc. A smaller condenser, made of iron and called *prolong*, is now fitted to the end of each clay tube to completely condense the zinc-vapour. Zinc vapour condenses partly as liquid in the clay tube and partly in the prolong where it is mixed with a little ZnO. The molten metal is raked out from time to time and cast into blocks. We thus get ingots of commercial zinc, called *spelter*.

Uses of lead :—Lead is used in making shots, bullets, plates for storage battery. It is employed for making Lead Chamber for manufactue of H_2SO_4. Evaporating pans, sinks and cisterns are also made from lead. Lead is employed for roofing-purposes. Lead-lined wooden vats are employed in manufacture of chemicals. Lead is also employed in the manufacture of pipes and sheaths for electric wires.

Two important *alloys* of lead are : (i) *type metal*, an alloy of Pb, Sn and Sb used in the manufacture of printing types and (ii) Soft solder, (an alloy of Pb and Sn), used for soldering.

Uses of tin :—Tin is used in preparing vessels of household and technical use ; for the manufacture of tin foils ; for "tinning". (i.e. giving a coating of tin to) copper and iron articles. Tin-amalgam is sometimes employed in the manufacture of mirrors.

Two important alloys of tin are : (1) *Common solder*, an alloy of lead and tin, employed for soldering and (2) *pewter*, an alloy of lead and tin, used for manufacturing cheap table-wares.

Uses of zinc :—Zinc is used in setting up electrical cells ; for galvanising iron ; in preparing alloys ; for extracting gold and silver ; and in the construction of gas-holders, pneumatic troughs, etc.

Two important alloys of zinc are : (1) *Brass*, an alloy of Cu and Zn, used in the manufacture of household utensils and cartridge cases, and (2) German silver, an alloy of Cu, Zn and Ni, used in the manufacture of household utensils and cheap ornaments,

Copper coin is also an alloy of Zn, containing copper and tin along with Zn.

Q. 7. *By what chemical test would you distinguish the following pairs of substances and identify each of them :—*

(a) Graphite and iodine, (b) a ferric and a ferrous salt, (c) a soluble sulphate and a soluble sulphide, (d) nitrous oxide and oxygen, (e) hydrobromic and hydriodic acid solutions ?

Ans. (*a*) Graphite is burnt in a current of pure oxygen and the gas formed is passed into lime-water, when lime-water turns milky, proving thereby that the gas is either carbon dioxide or sulphur dioxide. That the gas is not sulphur dioxide is proved by the fact that when it is passed into acidified potassium dichromate solution, the orange colour of the solution does not charge to green. Along with this chemical test, the physical characteristics also are to be taken into account in order to prove that the substance is graphite, *viz.*, its black colour, shining crystalline nature, and its soapy touch point to its being graphite.

Iodine is dissolved in potassium iodide solution and the solution so obtained is added to a solution of starch when the blue starch-iodine (absorption) compound is formed.

(*b*)

Reagents used	Ferric salt	Ferrous salt
1. NaOH solution	Brown precipitate of ferric hydroxide is formed.	Dirty green precipitate of ferrous hydroxide, turning brown in contact with air, is produced.
2. Potassium ferrocyanide, $K_4Fe(CN)_6$	A dark-blue precipitate of Prussian blue	A white precipitate is formed when ferrous salt is completely free from ferric salt.
3. Potassium ferricyanide, $K_3Fe(CN)_6$	No precipitate is formed, but only a brown coloration is produced.	A dark-blue precipitate of Turnbull's blue.
4. Ammonium thiocyanate, NH_4CNS	Blood-red coloration is produced.	No coloration is produced if the ferrous salt is completely free from ferric salt.

(*c*) A soluble sulphate in aqueous solution, when treated with barium chloride solution, produces a heavy white precipitate insoluble in conc. HCl, but a soluble sulphide does not undergo any such change.

A soluble sulphide in aqueous solution is made alkaline with caustic soda and then added a few drops of freshly prepared sodium nitroprusside solution, when colour of the solution turns purple-violet.

(*d*) Both nitrous oxide and oxygen are vigorous supporters of combustion, White *P* is ignited in a crucible floating on water and a jar of nitrous oxide is inverted over it. *P* continues to burn brilliantly and when the flame is extinguished the gas-jar is cooled, but water does not rise in the jar. But if instead of a jar of nitrous oxide, a jar of oxygen be used and the experiment carried out as before, on cooling, water is found to rise in the jar. In the former case an equal volume of nitrogen from nitrous oxide is set free and so prevents water from rising in the jar on account of its insolubility.

Moreover, by shaking the gas-jars, one containing nitrous oxide and the other containing oxygen, with alkaline pyrogallate solution, no colour change occurs in the case of nitrous oxide, but with oxygen the colour of the solution turns brown. Moreover, on inverting the jar of oxygen after shaking with alkaline pyrogallate over water, water rises in the jar and completely fills it up, showing that oxygen is completely absorbed by alkaline pyrogallate.

(*e*) *Distinction between HBr and HI can be drawn by adding :*

Reagents used	HBr solution	HI solution.
(1) $AgNO_3$ sol.	*Yellowish-white* ppt., of AgBr obtained, insoluble in HNO_3, but soluble with difficulty in NH_4OH	*Yellow* ppt. of AgI produced, insoluble in HNO_3, as also in NH_4OH.
(2) Chlorine water and CS_2 and shaking vigorously.	CS_2—layer at the bottom is coloured orange-yellow.	CS_2—layer at the bottom is coloured violet.

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FIRST PAPER

Q 1. *State Avogadro's hypothesis and discuss the evidence on which it is founded. What are the important deductions that can be made from it ?*

Ans. Avogadro's hypothesis states that "Equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain the same number of molecules."

The evidence on which this hypothesis is founded, is experimentally established by Gay Lussac's law of gaseous volumes. In order to explain the above law without bringing it into conflict with Dalton's Atomic theory, Avogadro enunciated the hypothesis mentioned above.

Gay Lussac experimentally established that when gases combine among themselves, they do so in simple numerical proportions by volume and the volumes of the reacting gases bear a simple relation to the volume of the resulting product, if that be gaseous, the volumes being all measured under the same conditions of temperature and pressure. Thus it is found by Gay Lussac that 1 volume of hydrogen combines with 1 volume of chlorine and forms two volumes of hydrochloric acid gas. Dalton's Atomic Theory failed to explain this simple behaviour of gases during combination. Though gases were found to obey the same laws relating to their volume, pressure and temperature and during combination a simple volumetric relationship was found to exist in them, yet a simple relationship existing between number of atoms present in equal volumes of all reacting gases, though stated by Berzelius, failed to explain experimentally established Gay Lussac's Law of Gaseous volumes. Avogadro saw the fallacy in the hypothesis put forward by Berzelius, *viz.*, *equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of atoms.* He differentiated between the ultimate particles of every type of matter, elementary and compound, capable of existing in the free state, retaining all the properties of that kind of matter of which it is a part, and the ultimate particles of elements which can take part in chemical reaction. He called the first type of particles *molecules* and the second type *atoms*. Molecules are divisible into atoms, but atoms are indivisible. This differentiation helped to explain Gay Lussac's Law of Gaseous volumes without bringing it into conflct with Dalton's Atomic theory. So the evidence on which Avogadro's hypothesis is based, is the experimentally established Gay-Lussac's Law of Gaseous volumes.

Thus, Gay Lussac's experimentally established fact is that 1 vol. of hydrogen combines with 1 vol. of chlorine to give 2 vols. of hydrogen chloride. From Avogadro's hypothesis it reduces to, n molecules of hydrogen combine with n molecules of chlorine to form 2n molecules of hydrogen chloride. Now, dividing out by *n*, 1 molecule of hydrogen combines with 1 molecule of chlorine to form 2 molecules of hydrogen chloride. So in forming 1 molecule of hydrogen chloride, half a molecule of hydrogen and half a molecule of chlorine will combine. Now, according to Avogadro, molecules can be subdivided, but atoms are indivisible. Now, if we take half a molecule to represent 1 atom, then it follows that 1 atom of hydrogen combines with 1 atom of chlorine to form 1 molecule of hydrogen chloride. So Dalton's Atomic Theory is also not violated.

The important deductions that can be made from the hypothesis are :

(*a*) Molecules of elementary gases like hydrogen, oxygen, nitrogen, chlorine, etc. are diatomic.

(*b*) Molecular weight of any gas is twice its density relative to hydrogen.

(*c*) The gram-molecular volume of all gases is the same under the same conditions of temperature and pressure and is 22·4 litres at N.T.P.

(*d*) Determination of the molecular formula of gas from its volumetric composition.

(*e*) Determination of the atomic weights of elements.

The two of the above deductions are made out in the following :—

(*a*) In discussing the formation of hydrogen chloride from hydrogen and chlorine, it has been shown that 1 molecule of hydrogen as also 1 molecule of chlorine contains at least 2 atoms of the elements mentioned.

Now, hydrogen present in the molecule of hydrogen chloride can be replaced by a metal like sodium *in one instalment* only, giving a normal salt ; and in no case, in more than one instalment. So we are led to believe that a molecule of hydrgen chloride contains 1 atom of hydrogen. Hence it follows from what has been stated before that 1 molecule of hydrogen consists of only two atoms of hydrogen.

(*b*) The density of any gas with respect to hydrogen is the ratio of the weight of a certain volume of that gas to the weight of the same volume of hydrogen, both the volumes being measured at the same temeperature and pressure.

Let D be the density of any gas relative to hydrogen. Then by definition, we have

$$D = \frac{\text{wt. of } V \text{ vols. of the gas}}{\text{wt. of } V \text{ vols. of hydrogen}} \quad \text{(under the same conditions of temperature and pressure)}$$

Let "n" be the number of molecules present in V vols. of the gas. Then, by Avogadro's hypothesis, we get

$$D = \frac{\text{wt. of ``}n\text{'' molecules of the gas}}{\text{wt. of ``}n\text{'' molecules of hydrogen}}$$

$$= \frac{n \times \text{wt. of 1 molecule of the gas}}{n \times \text{wt. of 1 molecule of hydrogen}}$$

$$= \frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 molecule of hydrogen}}$$

$$= \frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 2 atoms of hydrogen}}$$

[since hydrogen molecule is diatomic as proved under (*a*)]

$$= \frac{\text{wt. of 1 molecule of the gas}}{2 \times \text{wt. of 1 atom of hydrogen}}$$

$$\text{Hence } 2 \times D = \frac{\text{wt. of 1 molecule of the gas}}{\text{wt. of 1 atom of hydrogen}}$$

$$= \text{Molecular weight of the gas (by definition.)}$$

Q. 2. *How would you show experimentally that* **two** *volumes of hydrogen react with* **one** *volume of oxygen to yield* **two** *volumes of steam ? How do you identify water and distinguish it from other colourless liquids ?*

Ans. Experimentally the composition of steam is established by Hofmann's method. The apparatus for the purpose consists of a *U*-shaped eudiometer tube, one limb of which is closed and graduated. The closed end of the tube has near about the top two platinum wires sealed into the glass for passing sparks. The closed limb is surrounded by a wider jacket tube for circulating amyl alcohol vapour (B. P. 132°) when required. The other limb of the *U*-tube is open and is provided with a side-cock near the bottom.

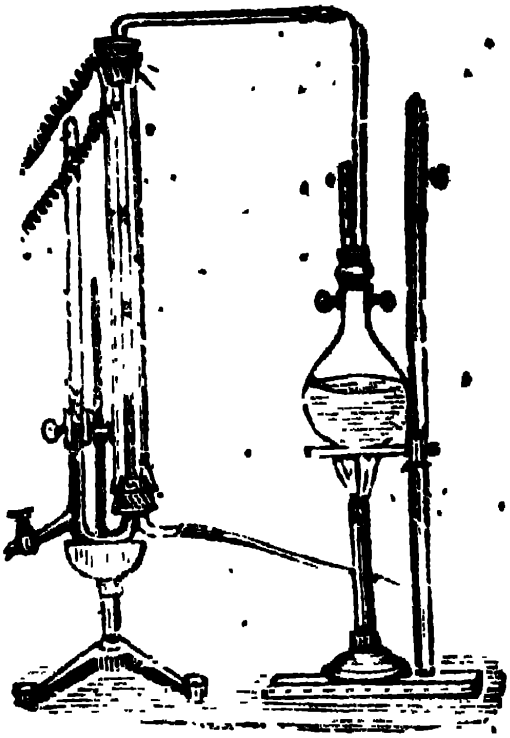


Fig. 101

The closed limb of the *U*-shaped tube is first filled with mercury and then by displacement of mercury it is partially filled with a dried mixture of 2 volumes of hydrogen and 1 volume of oxygen (obtained by the electrolysis of acidulated water and dried by conc. H_2SO_4). Vapour of amyl alcohol, obtained by boiling amyl alcohol in a flask as shown in the figure, is then made to circulate through the jacket tube and this passage of amyl alcohol vapour is continued upto the end of the experiment. Then, after some time, when the temperature of the mixed gases becomes constant, the mercury level in both the limbs is adjusted to the same height and the volume of the mixture is carefully read off. Some mercury is then run out by opening the tap to reduce the pressure.. The open end is then closed with the thumb and a single electric spark is passed through the gas mixture by connecting the two platinum wires sealed in the glass of the closed limb to the terminals of an induction coil. Hydrogen and oxygen combine to produce steam. Mercury level is again adjusted to the same height in both the limbs and the volume occupied by steam is noted carefully. It will be found that the steam produced occupies exactly two-thirds of the volume occupied by the mixture of hydrogen and oxygen. That the residual volume of gaseous product is of steam only is proved by discontinuing the passage of amyl alcohol vapour through the jacket and allowing the temperature of the closed limb of the eudiometer tube to come down gradually to room temperature. It is found that mercury gradually rises in the closed limb and ultimately fills it up completely, since condensed water occupies negligible volume.

Water can be identified by adding it to anhydrous copper sulphate which is white in colour, when the white amorphous material will change into a blue crystalline substance. Water can be distinguished from other colourless liquids by the observation of its freezing point and its boiling point. Pure water freezes at 0°C. and boils at 100°C. under normal atmospheric pressure, *viz.*, pressure of 760 mm. of mercury.

Q. 2. Alternative :

Define and illustrate : (a) Equivalent of an element, (b) equivalent of a compound, (c) gram-atom, (d) gram-molecule, (e) normal solution.

Ans. (*a*) Equivalent of an element is a number which expresses that so many parts by weight of it combine with or displace from a compound 1 part by weight of hydrogen, or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine. Mathematically expressed

Equivalent of an element

$$= \frac{\text{wt. of the element in certain unit}}{\text{wt. of hydrogen displaced by or combined with the given weight of the element expressed in the same unit.}}$$

So it, being the ratio of two weights, is a mere number.

Thus 12 parts by weight of magnesium can displace 1 part by weight of hydrogen.

Hence 12 is the equivalent of magnesium.

(*b*) Equivalent of a compound indicates that amount of it which contains one equivalent of the active element present in it. Thus the equivalent of anhydrous sodium carbonate, Na_2CO_3, is that amount of it which contains one equivalent of the active element sodium in it. Now 23 is the equivalent of sodium and that amount of sodium is present in $\frac{106}{2}$ or 53 parts by weight of anhydrous Na_2CO_3. Therefore 53 is the equivalent of anhydrous sodium carbonate.

(*c*) The atomic weight of an element expressed in grams is called a gram-atom of the element. Thus, one gram-atom of sodium indicates 23 grams of sodium.

(*d*) The molecular weight of an element or a compound expressed in grams is known as a gram-molecule of the element or the compound mentioned. Thus, one gram-molecule of chlorine stands for 71 grams of chlorine ; one gram-molecule of sodium chloride stands for 58·5 grams of sodium chloride.

(*e*) A normal solution of any substance is that which contains one gram-equivalent of that substance, *i.e.*, equivalent of the substance expressed in grams, dissolved in a litre of the solution.

Thus, 36·5 grams is the gram-equivalent of hydrochloric acid. Therefore when 1 litre of a solution of hydrochloric acid contains 36·5 grams of hydrochloric acid, it is a normal solution of hydrochloric acid.

Q. 3. *Describe the preparation of* **dry** *ammonia gas in the* **laboratory**. *Give a sketch of the apparatus you would use. Outline its important physical and chemical properties. With what uses of ammonia are you acquainted ?*

Ans. Preparation of *dry* ammonia in the *laboratory* is carried out by heating *dry* powdered ammonium chloride with about twice its weight of powdered quicklime in a hard glass test-tube closed by a cork through which a delivery tube is fitted. The hard glass test-tube is clamped in a slightly inclined position to a retort stand and the delivery tube is joined to the bottom of a lime-tower, filled with quicklime, as shown in the figure. An upright delivery tube is next fitted to the top of the lime-tower as shown in the figure. Ammonia, evolved and dried in lime-tower, is collected by downward displacement of air.

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

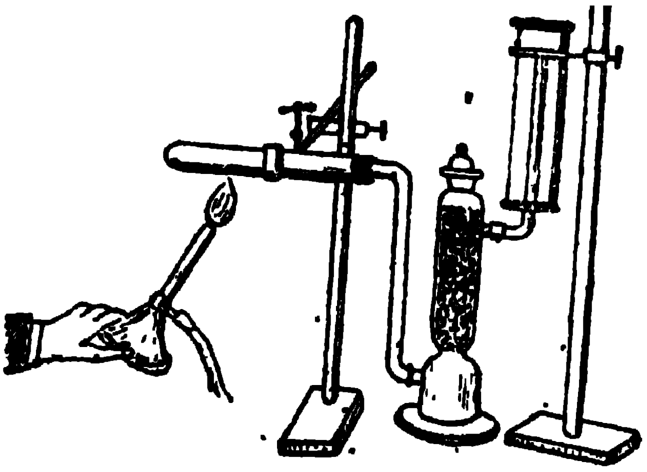


Fig. 102

Properties of ammonia :— It is a colourless gas with a peculiar pungent smell. It is lighter than air and is extremely soluble in water.

Ammonia is neither a supporter of combustion nor combustible in air. But when the gas is set fire to in an atomsphere of oxygen it burns with a yellowish flame.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

The aqueous solution is alkaline and is soapy to the taste, and so it is supposed to contain ammonium hydroxide, which has not been isolated, for on boiling the aqueous solution, ammonia is completely expelled.

$$NH_3 + H_2O = NH_4OH.$$

The aqueous solution of ammonia can neutralise acids and can precipitate the hydroxides of many metals when added to the solution of their salts.

When ammonia is passed over heated metallic sodium or potassium, the amide of the alkali metal is formed and hydrogen is evolved.

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

Ammonia acts as a reducing agent under certain conditions. Thus, when ammonia is passed over heated copper oxide or lead oxide, metallic copper or lead is formed.

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2.$$

Ammonia in excess reacts with chlorine and is oxidised to nitrogen, the reaction taking place in two stages, *viz.*,

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

$$6HCl + 6NH_3 = 6NH_4Cl.$$

But with excess of chlorine, nitrogen trichloride is formed.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

Use of ammonia :—

Aqueous solution of ammonia is used as a reagent in the laboratory and is also employed as a detergent for washing out grease. In medicine also the dilute solution of ammonia is used. Ammonia as a gas is employed in the manufacture of sodium carbonate by Solvay's process, as also in the production of ammonium sulphate which is employed as a valuable fertiliser. Liquid ammonia is used as a refrigerant in the manufacture of ice.

Q. 4. *Give a brief account of the manufacture of sulphuric acid by the* **Chamber process.** *Explain the reactions involved. Give* **two** *illustrations of the use of sulphuric acid as (a) a dehydrating agent, (b) an oxidising agent.*

Ans. For a diagrammatic sketch of the *Chamber Plant* see Q. 2, Alternative, Second Paper, 1952.

Description of the Process :—The gases from the pyrites burners consisting of sulphur dioxide (produced by the burning of pyrites, FeS_2, or sulphur in the burner : $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$) and air are allowed to enter the nitre ovens in which sodium nitrate and conc. sulphuric acid are heated together to give nitric acid. Thus a mixture of air, SO_2, HNO_3 vapour and oxides of nitrogen is obtained. This mixture is next passed up the Glover tower and there it meets a downward current of a mixture of *Chamber acid* and *nitrated* sulphuric acid. The gas-mixture is thus cooled and a certain portion of sulphur dioxide is converted into H_2SO_4. At the same time the Chamber acid is concentrated by loss of water and the nitrated H_2SO_4 is freed from oxides of nitrogen. The gas-mixture, coming out of the Glover's tower, enters lead chambers arranged one after another and meets there with fine spray of water, injected inside the chambers from the roofs of the chambers and atomised by impact with a metal plate. H_2SO_4 is produced inside the chambers and collects on the floor of the chambers. This is known as *Chamber acid*, which is collected underneath in a tank and pumped up to the top of the Glover tower. The gases escaping from the last lead chamber are charged with oxides of nitrogen and for recovery of these oxides of nitrogen the gas-mixture is passed up the Gay Lussac's tower where it meets a downward current of conc. H_2SO_4 which takes up the oxides of nitrogen. The spent gases are next allowed to escape to the atmosphere through a chimney (not shown in the figure).

Reactions occuring in Glover's tower and in lead Chambers :—

(1) $SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$
(2) $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$
(3) $2NO + O_2 = 2NO_2$

When steam or cold water supply falls short in lead chambers, the following reaction takes place with formation of "Chamber crystals" :—

$$3NO_2 + 2SO_2 + H_2O = NO + 2SO_2(OH)(NO_2)$$

Nitrosyl sulphuric acid, or chamber crystals.

When water is introduced in sufficient quantity, chamber crystals decompose producing sulphuric acid :—

$$2(SO_2)(OH)(NO_2) + H_2O = 2H_2SO_4 + N_2O_3$$
$$N_2O_3 = NO + NO_2.$$

(*a*) (*i*) Sulphuric acid in the concentrated form can remove moisture present in a moist gas. For example, when hydrogen is prepared by the action of dilute sulphuric acid on zinc, the gas evolved is rendered moist by the water-vapour escaping along with the gas. The evolved hydrogen, when passed through a wash-bottle containing conc. H_2SO_4, is freed from moisture and rendered dry.

(*ii*) Conc. H_2SO_4 can also abstract the elements of water from compounds where hydrogen and oxygen are present in the same proportion as in water. Thus, cane-sugar $C_{12}H_{22}O_{11}$, when in the form of a concentrated solution, is treated with conc. H_2SO_4, carbon is produced, water being abstracted by conc. H_2SO_4.

$$C_{12}H_{22}O_{11} = 12C + 11H_2O.$$

(*b*) (*i*) Concentrated sulphuric acid, when heated with potassium bromide, oxidises KBr to bromine.

$$2KBr + 3H_2SO_4 = 2KHSO_4 + SO_2 + Br_2 + 2H_2O.$$

(*ii*) When heated with carbon, concentrated sulphuric acid oxidises carbon to carbon dioxide, itself being reduced to sulphur dioxide.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.$$

Q. 4. Alternative.

What do you understand by the term **'allotropy'** *?*

Describe some experiments to prove that **red** *and* **yellow** *phosphorus are allotropic forms of the same element? How are* **yellow** *and* **red** *phophorus obtained from* **bone-ash** *?*

Ans. Allotropy is the property possessed by an element of occurring in two or more forms; the forms differ entirely in physical and to some extent in chemical properties.

Experiments to prove that red and yellow phosphorus are allotropic forms of the same element :—

(1) Equal weights of red phosphorus and yellow phosphorus are taken and burnt carefully in excess of oxygen by suitable arrangement so that there is no loss of the products formed in each case. The products are collected separately and dissolved in excess of water, whereby phosphoric acid, H_3PO_4, is formed in both the cases. The two different solutions so obtained are neutralised with ammonia and completely precipitated separately with magnesia mixture in presence of ammonia and ammonium chloride. The precipitates are filtered separately, washed thoroughly, transferred to a weighed crucible, ignited completely to magnesium pyrophosphate and weighed to constant weight by repeated heating, cooling in a desiccator and weighing.

It will be found, if the experiment be carefully performed, that the two weights of magnesium pyrophosphate obtained in the two cases are the same, proving thereby that we are dealing with one and the same element.

(2) When red phosphorus in heated in an inert atmosphere above 550°C. so that vapours are produced and the vapours so formed are rapidly cooled, yellow phosphorus is obtained. Again, if yellow phosphorus be heated to 240°C. in an inert atmosphere with a trace of iodine (catalyst), red phosphorus is formed. This inter-convertibility shows that yellow phosphorus and red phosphorus are allotropic forms of the same element.

Preparation of yellow phosphorus from bone-ash :—Bone-ash mainly consists of calcium phosphate (80%) and is utilised for getting yellow phosphorus. The old *Retort Process* is now obsolete and the modern *Electrical Process*, devised by Readman, Parker and Robinson, is now in vogue for getting yellow phosphorus.

A mixture of bone-ash, sand and coke is fed through the hopper, by a worm conveyer into a closed electric furance which is made of brick-work. The furance is provided with an outlet near the top for the escape of hot gases and vapours of phosphorus, and another at the bottom for taking out the slag. Electric current is supplied through two stout carbon rods fixed a little above the bottom level as shown in the figure so as to form an "arc" inside the mixture which is heated very strongly in this way to about 1200° – 1500°C.

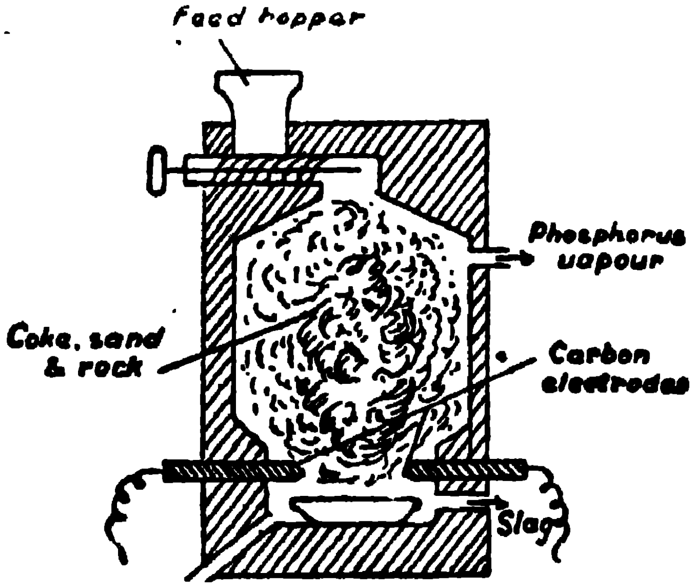


Fig. 103

At the high temperature produced inside the mixture calcium phosphate reacts with silica, producing calcium silicate and phosphorus pentoxide.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

Phosphorus pentoxide is then reduced by carbon of coke and phosphorus is set free.

$$2P_2O_5 + 10C = 10CO + 4P.$$

Calcium silicate melts and sinks to the bottom and therefrom it is run off by the slag-hole. Phosphorus vapours along with CO escape through the outlet near the top, and are passed into water, where phosphorus vapours condense into solid yellow phosphorus and carbon monoxide, being insoluble, escapes as gas.

Fresh mixture is introduced from time to time and the process is thus made continuous.

Red phosphorus is obtained from yellow phosphorus which is directly obtained from bone-ash by the method described above. Yellow phosphorus is heated to 240° − 250°C. out of contact with air, in a covered cast-iron vessel provided with a safety tube with a trace of iodine. The temperature is not allowed to rise above 250°C. The solid, left in the vessel after heating, is first ground to powder, and then boiled with caustic soda solution to remove any unchanged yellow phosphorus likely to be present. The residue is finally washed with water and dried.

Q. 5. *What is lime? How is it obtained? What happens when lime is (a) mixed with water, (b) heated strongly with sand, (c) treated with chlorine, and (d) exposed to carbon dioxide gas? Give equations.*

Ans. Common lime is also called quicklime and it is chemically oxide of calcium, CaO. It is obtained by heating limestone or shells of the molluscs in specially designed kilns. The operation is known industrially as lime-burning and is carried out in the continuously-acting furance constructed as shown in the adjoining figure. A vertical shaft furance made of bricks with a hopper at the top is used herein. The fire-place is situated by the side of the furnace, and several openings are present at the top of the furnace and on the side opposite to the fire-place there is an arrangement for an opening closed with clay for removing the lime formed by the operation by removing the clay-covering and then again closing it up with clay for the

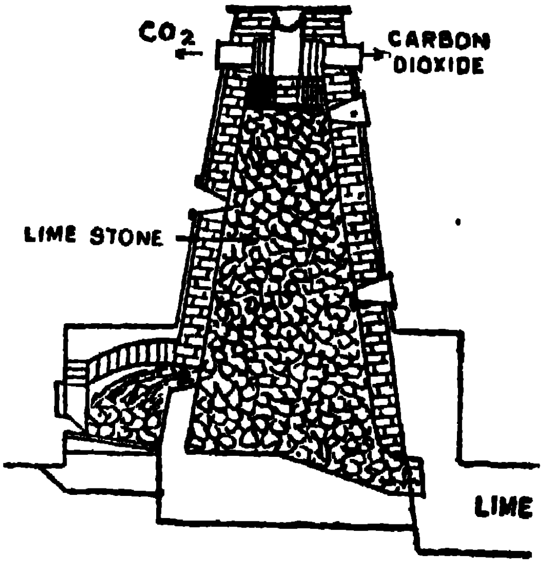


Fig. 104

the subsequent operation. Limestone is charged into the furnace through the hopper and the flames and hot gases from the fire-place where producer gas is burnt are made to play on the limestone. Carbon dioxide is evolved and escapes through the outlet at the top. Quicklime is then raked out by opening the outlet at the bottom. Fresh charge of limestone is next introduced at the top through the hopper and so the process is made continuous.

$$CaCO_3 = CaO + CO_2.$$

(*a*) Quicklime crumbles to powder on addition of small quantity of water and great heat is developed and a hissing sound is produced ; a portion of water escapes as steam. When the required amount of water is added, complete conversion to a dry white powder of calcium hydroxide occurs, due to chemical combination of quicklime with water. This process of conversion of quicklime to calcium hydroxide is known as *slaking of lime.*

$$CaO + H_2O = Ca(OH)_2.$$

On addition of a large quantity of water a small portion of calcium hydroxide passes into solution and the large portion of $Ca(OH)_2$ forms an emulsion with water. The solution of $Ca(OH)_2$ obtained by filtration is known as *lime-water* and the emulsion of $Ca(OH)_2$ with water is known as *milk of lime.*

(*b*) When strongly heated with sand or silica (SiO_2), quicklime combines with SiO_2 forming a fusible calcium silicate.

$$CaO + SiO_2 = CaSiO_3.$$

(*c*) Chlorine does not react with quicklime at ordinary temperature, but when chlorine is passed over red-hot quicklime, oxygen is evolved and calcium chloride is formed.

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$

(*d*) When exposed to *dry* carbon dioxide gas, quicklime slowly absorbs CO_2 when a sufficient excess of the gas is present and calcium carbonate is formed. If the carbon dioxide gas be moist, then quicklime readily absorbs CO_2 with the formation of calcium carbonate.

(*i*) $CaO + CO_2 = CaCO_3.$
(*ii*) $CaO + H_2O = Ca(OH)_2$
(*iii*) $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$

Q. 5. Alternative :

Name the important minerals of aluminium and give their formulae. How is metallic aluminium obtained from the oxide ore? State uses of the metal.

How is anhydrous aluminium chloride prepared? Describe the action of caustic alkali on metallic aluminium.

Ans. The important minerals of aluminium are

(1) *Corundum, ruby, sapphire* etc., Al_2O_3
(2) *Diaspore,* Al_2O_3, H_2O
(3) *Bauxite,* Al_2O_3, $2H_2O$
(4) *Gibbsite,* Al_2O_3, $3H_2O$

(5) *Potash-felspar, Orthoclase,* K_2O, Al_2O_3, $6SiO_2$, which, on weathering, gives rise to *Porcelain-clay, China-clay* or *Kaolin*, Al_2O_3, $2SiO_2$, $2H_2O$.

(6) *Cryolite,* AlF_3, $3NaF$.
(7) *Alunite,* K_2SO_4, $Al_2(SO_4)_3$, $4Al(OH)_3$,
(8) *Spienel* MgO, Al_2O_3.
(9) *Chrysoberyl,* BeO, Al_2O_3.

The extraction of aluminium from its oxide ore consists of two operations :—(a) Purification of Bauxite which contains ferric oxide and silica as impurities and (b) electrolytic decomposition of purified Bauxite.

(*a*) Purification of Bauxite with the production of pure Al_2O_3 can be carried out in two ways. In the old process, (a) bauxite is heated to bright redness with sodium carbonate, when sodium aluminate, $NaAlO_2$, is formed. The mass is rapidly lixiviated with water, whereby a solution of sodium aluminate is obtained and finely divided ferric oxide, which remains insoluble, is removed by decantation. The clear solution of sodium aluminate is then treated with carbon dioxide at 50° – 60°C., when a granular precipitate of aluminium hydroxide is thrown down.

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2$$
$$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3.$$

The precipitated $Al(OH)_3$ is separated and then ignited when Al_2O_3 is obtained.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

(*b*) In the modern Baeyer process, the calcined bauxite is digested under 80lb. pressure and at 150°C. with caustic soda solution. Sodium aluminate is formed and oxide of iron is left behind. The solution of sodium aluminate is separated from deposited iron oxide by decantation, and then agitated with a small quantity of freshly precipitated alumina. Nearly all the alumina in solution is thereby precipitated which is easily washed and this on ignition yields pure Al_2O_3.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O.$$

The above reaction is reversed on agitation with precipitated Al_2O_3.

The alumina purified by any of the above processes is then dissolved in fused cryolite and electrolysed between carbon electrodes. The electric furnace consists of an *iron box* lined internally with blocks of gas carbon and is made the cathode. The anodes consist of a bunch of carbon rods hung from a copper rod and dipped into the electrolytic bath. The electrolyte is a solution of purified Al_2O_3 in fused cryolite, AlF_3, $3NaF$, together with some fluorspar, CaF_2, the temperature of the bath being kept at 875° – 950°C.

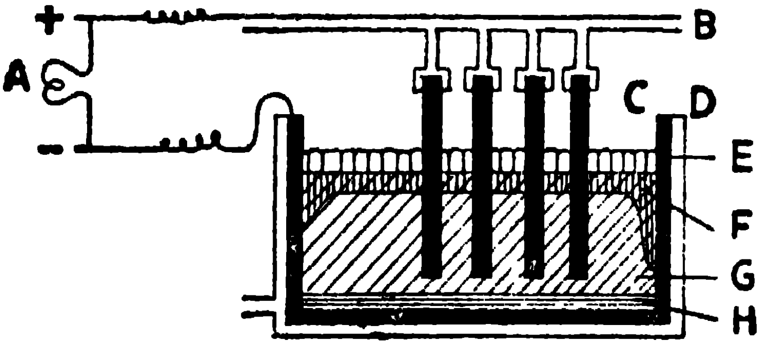


Fig. 105

The alumina is electrolysed, the metal being deposited at the bottom of the bath below the anodes. The oxygen liberated at the anodes attacks them with the production of CO and CO_2 in about equal volumes. The charge is usually covered with a layer of carbon and fresh alumina is stirred in from time to time. The complete decomposition of alumina is indicated by a rise in resistance of the bath, the lamp shunted with the bath brightening at this stage.

$$2Al_2O_3 = 4Al + 6O_2$$
$$C + O_2 = CO_2$$
$$2C + O_2 = 2CO.$$

The chief uses of the metal are

(1) in the production of light alloys like magnalium (Al + Mg), duralumin (Al + Mg + Cu + Mn), aluminium-bronzes, etc. ;

(2) in the production of aluminium powder which is used as a paint and in fire works ;

(3) in the *thermite* process of the extraction of metals like Cr, Mn and for repairing iron rails ;

(4) in the production of amalgamated aluminium foil which is used as a reducing agent in neutral medium ;

(5) in the production of cables and overhead wires for transmission of electric current.

Anhydrous aluminium chloride is prepared by heating a mixture of aluminium oxide and carbon in a hard glass tube and passing a current of dry chlorine gas over the mixture. The exit tube fitted to the hard glass tube is introduced through a cork into a dry wide-mouthed bottle and anhydrous $AlCl_3$ collected therein by sublimation.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

When metallic aluminium is heated with caustic alkali (either caustic soda, NaOH, or caustic potash, KOH), hydrogen gas is evolved and sodium or potassium aluminate, $NaAlO_2$ or $KAlO_2$ is formed.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$
$$2Al + 2KOH + 2H_2O = 2KAlO_2 + 3H_2.$$

SECOND PAPER—1954

Q. 1. *State Faraday's laws of electrolysis and express them in the form of an equation. Calculate at N.T.P., the volume of hydrogen which will be liberated when a current of 10 amperes is passed through a dilute solution of* H_2SO_4 *in water for 6 minutes and 26 seconds. Given one Faraday = 96,500 coloumbs.*

Ans. (*a*) Faraday's laws of electrolysis are two in number. (*i*) The mass of an ion liberated during electrolysis is directly proportional to the strength of the current and to the time during which the current flows i.e., to the quantity of electricity flowing through the circuit.

Thus if W be the mass in gram of an ion liberated, C the strength of the current in ampere and t the time in second during which the current flows, then $W \propto C \times t$, or $W = ZCt$. where Z is a constant. Now when $C = 1$ amp., and $t = 1$ sec. then $W = Z =$ mass of ion liberated by unit quantity of electricity. This quantity, Z, is called the electro-chemical equivalent of the substance liberated by the passage of unit quantity of electricity.

(*ii*) When the same quantity of electricity is passed through different electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.

Thus from the 2nd law it follows that the electro-chemical equivalent (E. C. E.) of an element is directly proportional to its chemical equivalent (C. E.). Thus

$$\frac{\text{E. C. E. of an element } X}{\text{E. C. E. of another element } Y} = \frac{\text{C. E. of } X}{\text{C. E. of } Y}$$

Hence, $$\frac{\text{E. C. E. of any element}}{\text{E. C. E. of hydrogen}} = \frac{\text{C. E. of the element}}{\text{C. E. of Hydrogen}}$$

But the C. E. of hydrogen $= 1$

$\therefore$ E. C. E. of any element $=$ E. C. E. of Hydrogen $\times$ C. E. of the element.

From the 1st law, we deduce the relationship $W = ZCt$, the notations being explained before.

From the 2nd law, we get the relationship, electro-chemical equivalent of an element (or ion) $=$ Electro-chemical equivalent of hydrogen $\times$ chemical equivalent of the element (or ion).

Hence, by combining these two laws, we get the mathematical relationship

$W = H \times E \times C \times t$, where

$W =$ mass of an element (or ion) in gram liberated,

H = electro-chemical equivalent of hydrogen ;

$E =$ chemical equivalent of the element (or ion) ;

$C =$ strength of the current in amperes ;

$t =$ time measured in seconds.

According to Faraday's Second Law of Electrolysis, 1 Faraday or 96,500 coloumbs of electricity will liberate equivalent weight of the element in grams.

Thus 1 Faraday of electricity will liberate 1 gram of hydrogen, *i.e.*, 96,500 coloumbs or 96,500 amperes of current flowing for 1 second will liberate 1 gram of Hydrogen. Therefore 1 ampere of current flowing for 1 second will liberate $\frac{1}{96,500}$ gm. of Hydrogen, and this is the electro-chemical equivalent of Hydrogen by definition.

Hence, from the relation

$W=Zct$, where W = the mass of Hydrogen liberated due to the passage of current c amperes flowing for t seconds, Z being the electro-chemical equivalent of Hydrogen, we have

$$W=\frac{1}{96,500}\times 10\times 386 \text{ gm.}$$

[∵ 6 mins. 26 secs, = 386 secs.]

Now, we know that the molecular weight of Hydrogen expressed in grams occupy 22·4 litres at N.T.P.

Therefore 1 gram of Hydrogen will occupy 11·2 litres at N.T.P.

Hence the volume of Hydrogen liberated at N.T.P. by the current of 10 amperes flowing for 6 mins. 26 secs.

$$=\frac{1}{96,500}\times 10\times 386\times 11{\cdot}2 \text{ litres}$$

$$=448 \text{ c. c.}$$

Q. 2. *Discuss the criteria of a chemical compound. Describe how you would separate the constituents of a mixture consisting of sulphur, sodium chloride and sand in a fine state of division.*

Ans. A chemical compound is homogeneous in character and possesses fixed properties which are characteristics of that particular substance. It is produced by chemical action between two or more elements and compounds and it differs entirely in properties from the elements or compounds from which it is formed. It possesses a fixity in composition and its formation is always attended with a heat change (either evolution or absorption of heat). A chemical compound can therefore be broken up into two or more different elements or compounds by chemical means.

Thus, water is a chemical compound formed by the chemical union of two gaseous elements, Hydrogen and Oxygen. The properties of water are entirely different from the properties of either Hydrogen or Oxygen. Hydrogen and Oxygen are present in water, which is homogeneous in character, in definite proportions by weight, *viz.*, 2 parts of Hydrogen are always found to be combined with 16 parts by weight of Oxygen in water molecule. The combination of Hydrogen and Oxygen is always attended with evolution of definite quantity of heat in the formation of water. Also water can be broken up into its elements *viz.*, by the passage of electricity through acidulated water.

The mixture consisting of sulphur, sodium chloride and sand in a fine state of division, is first boiled with water and filtered. The residue on the filter paper is washed with hot water till the filtrate is entirely free from sodium chloride (as tested by silver nitrate solution when no turbidity is produced). The filtrate, collected in a basin, is evaporated to dryness and sodium chloride recovered in the solid state. The residue is dried completely by placing it in a steam oven, then treated repeatedly with warm carbon disulphide and filtered.

The filtrate is collected in another shallow basin. The treatment with warm CS_2 is continued till all the sulphur passes into solution. The CS_2 from the filtrate is evaporated away by exposing it to the atmosphere and sulphur recovered. The residue on the filter paper is sand.

Q. 3. *State the reactions which occur when (a) steam is passed over heated iron powder, (b) CO_2 is passed in excess through a concentrated solution of NaCl saturated with ammonia, (c) NH_3 is passed in excess through a suspension of calcium sulphate saturated with CO_2 under pressure, (d) H_2S is passed through a suspension of iodine in water.*

Ans. (*a*) Steam is decomposed, Hydrogen is evolved and iron is oxidised to triferric tetroxide. The iron powder should be red-hot.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

(*b*) This reaction is the basis of the ammonia-soda process for the manufacture of sodium carbonate. NaCl is converted into sodium bicarbonate by the simultaneous action of ammonia and CO_2,

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

On account of the low solubility of $NaHCO_3$, it is precipitated out.

(*c*) The reaction gives rise to the formation of ammonium sulphate solution and calcium carbonate formed simultaneously remains insoluble.

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4.$$

(*d*) Iodine is reduced to hydriodic acid and H_2S is oxidised to sulphur.

$$H_2S + I_2 = 2HI + S.$$

Sulphur is precipitated and hydriodic acid remains in solution.

Q. 4. Alternative :

Starting from sodium chloride, how caustic soda and chlorine can be manufactured ? State two important uses of each of the products ?

Ans. Sodium chloride solution (brine) is electrolysed in a divided cell in order to get caustic soda and chlorine.

The electrolysis of brine is carried out in a rectangular vessel divided into three compartments by means of slate partitions (Fig. 106). The partitions do not actually touch the bottom of the vessel but dip into a layer of mercury which covers its floor. The two outer compartments are filled with *brine* and are fitted with stout carbon rods which serve as the **anodes.** The **cathodes** are a bunch of iron rods suspended in the middle compartment containing water to which a little caustic soda has been added to make it a conductor. The layer of mercury is electrically connected with the iron rods. The whole vessel rests, on one side, upon an eccentric. The anodes are now connected together and then with the positive pole of a battery, while the cathode is connected with its negative pole. On passing electric current chlorine is evolved at the anodes and is led away for the manufacture of bleaching powder. Sodium is liberated at the mercury cathode in the outside compartments where it dissolves in

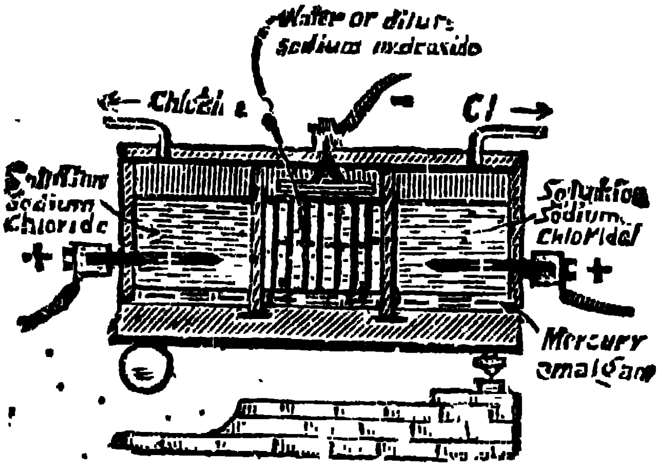


Fig. 106

mercury producing an amalgam. The amalgam is transferred to the middle compartment by giving a slow rocking movement to the whole vessel by the eccentric. Sodium reacts with water producing caustic soda and hydrogen. Caustic soda solution is now taken out and is evaporated in iron vessels. The solid so obtained is finally melted down and cast into sticks, pellets or balls.

$$2Na + 2H_2O = 2NaOH + H_2.$$

Uses of caustic soda.—Caustic soda is employed (1) in the manufacture of soap, metallic sodium and many chemicals ; (2) in the manufacture of paper and artificial silk ; (3) in bleaching and refining oils ; (4) in the purification of bauxite and (5) in the laboratory as a reagent.

Chlorine is evolved during this manufacture of caustic soda at the anodes which is led off by an outlet pipe, and collected over brine. For industrial purpose it is dried by conc. H_2SO_4, liquefied and the liquid is stored in iron cylinders.

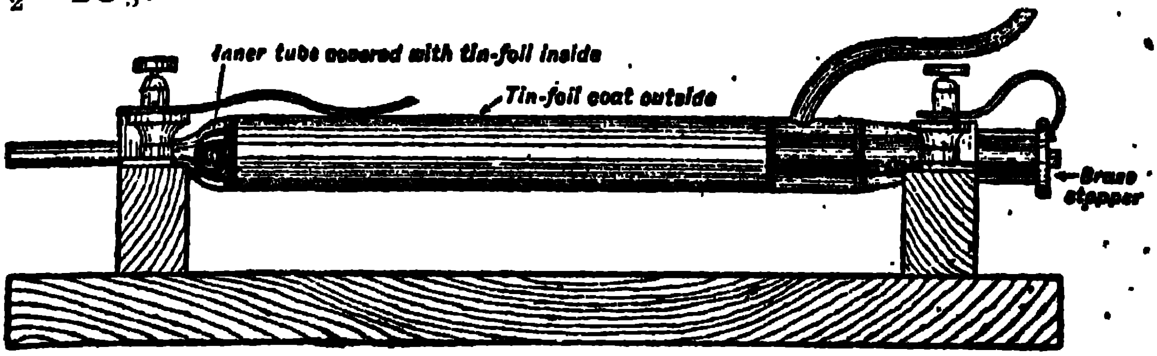
Uses of Chlorine :—

Chlorine is used in the manufacture of bleaching powder, chloroform, bromine, chlorates, etc., as a disinfectant, for preparing pure HCl and for preparing certain poisonous gases like phosgene, mustard gas, etc., in the extraction of gold and for refining petroleum.

Q. 4. *Describe how you would prepare ozone. Sketch the apparatus. How would you obtain it in a fairly pure state ?*

State its uses. Describe what happens when ozone is passed through (a) hydrogen peroxide, (b) acidified potassium iodide solution and (c) potassium permanganate solution. Give equations.

Ans. Preparation of Ozone :—Ozone is best obtained by exposing pure dry oxygen to the action of silent electric discharge in Siemen's ozoniser which consists of two concentric glass tubes. The outer tube is coated outside and the inner lined inside with tinfoils. These tinfoils are connected with two binding-screws which in their turn are in connection with a Ruhmkorff's coil. Dry oxygen is passed through the annular space in slow stream and a series of silent electric discharge is passed. The gas coming out at the exit consists of a mixture of oxygen and ozone. $3O_2 = 2O_3$.



Siemens' ozoniser.

Fig. 107

The yield of ozone is only 5 to 8%.

Ozone can be prepared in a fairly pure state by the following method :—

Ozonised oxygen that is produced by the method described is liquefied by taking it in a tube and immersing that tube in liquid air. A blue liquid is obtained, which is a solution of liquid ozone in liquid oxygen. This liquid is strongly cooled and then allowed to evaporate by lowering the pressure, when violet black crystals of pure solid ozone are formed. These crystals are then separately taken, and the temperature is allowed to rise gradually when the solid ozone first melts and the liquid so formed begins to boil at −112·4°C., yielding a dark-blue gas which is pure ozone.

(*a*) Oxygen is evolved as gas and water is left behind.

$$H_2O_2 + O_3 = H_2O + 2O_2.$$

(*b*) Iodine is liberated and the colour of the solution turns brown.

$$O_3 + 2KI + H_2SO_4 = O_2 + I_2 + K_2SO_4 + H_2O.$$

(*c*) The solution remains unchanged in colour. Ozone does not react with potassium permanganate ($KMnO_4$) at all.

Q. 4. Alternative :

What experiments have been made with the object of isolating fluorine? How do you account for their failure? How and by whom flourine was isolated for the first time? How is hydrogen fluoride prepared in a state of purity and what are its uses?

Ans. The following were the experiments made for isolating fluorine, with the reasons for their failures :—

(1) Hydrofluoric acid was heated with strong oxidising agents like manganese dioxide, potassium permanganate, etc., but no fluorine was obtained because hydrofluoric acid cannot be oxidised in that way, since fluorine was most reactive and the most electro-negative element known.

(2) Aqueous solution of hydrofluoric acid was subjected to electrolysis, but no fluorine was evolved : instead Oxygen was liberated at the anode. This was due to decomposition of water by electricity which was rendered conducting due to the presence of HF.

(3) Anhydrous HF was next attempted to be electrolysed, but it was found to be a perfect non-conductor of electricity.

Fluorine was isolated by Moissan in 1886 by the anodic oxidation of HF in a bath of anhydrous HF containing potassium hydrogen fluoride dissolved in it.

Preparation of Fluorine by Moissan's method :—Fluorine is prepared by the electrolysis of a solution of potassium hydrogen fluoride, KF, HF in anhydrous hydrofluoric acid, HF. The apparatus consists of a U-tube made of an alloy of Platinum-Iridium provided with two side tubes and is fitted with fluorspar stoppers. Two electrodes made also of Platinum-Iridium alloy and thickened at the bottom pass through these fluorspar stoppers. The whole apparatus is kept immerged in a bath of boiling methyl chloride at about-23°C. The U-tube is $\frac{2}{3}$rd filled up with the electrolyte, a solution of KF, HF in anhydrous HF. On passing the current through the electrolyte, HF undergoes decomposition, H_2 being liberated at the cathode and Fluorine at the anode. The fluorine is led through a spiral of Pt kept immersed in boiling methyl chloride to remove any HF vapour by condensation. The gas is next passed through a tube of Pt packed with NaF which removes the last trace of HF. Fluorine is collected in a Pt vessel by the upward displacement of air.

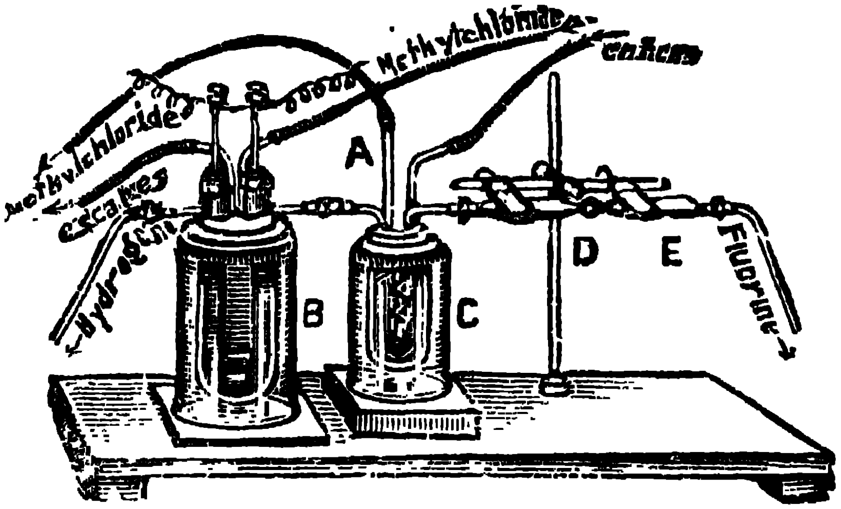


Fig. 168

Pure hydrogen fluoride is prepared by heating anhydrous potassium hydrogen fluoride (Fremy's salt, KHF_2) in a platinum retort connected to a platinum condenser and a platinum receiver.

Ice-cold water is made to circulate in the condenser and the receiver is placed in freezing mixture. Pure HF collects in the receiver. $KHF_2 = KF + HF$.

The last trace of moisture from the distillate is removed by dipping two platinum electrodes in the liquid distillate and passing electric current through it. As soon as all the water is removed by electrolysis with the evolution of H_2 and O_2 at the two electrodes, the passage of current is stopped.

Uses of HF :—(1) Hydrofluoric acid is used extensively for etching glass. All the glass measuring-instruments are marked by etching with HF.

(2) It is used in the laboratory for analysis.

(3) It is employed for removing silica from iron-castings.

(4) It is also used for sterilising casks in which brewing operations for production of alcohol are carried out.

Q. 5. *What are the three important commercial varieties of iron and how do they differ from one another in their composition and properties ? State their uses.*

Describe the production of one of these varieties of iron starting from iron ores (oxide).

What happens when metallic iron is placed in a solution of copper sulphate ? Give equation.

Ans. Three important commercial varieties of iron are : cast iron, wrought iron and steel.

Cast-Iron, Wrought Iron and Steel Compared :—

Properties.	Cast Iron	Wrought Iron	Steel
Carbon content	2 - 5%	0·12 - 0·25%	0·25 - 1·5%
Impurities	Also impurities like Si, Mn, P, S etc. are present	Purest form of commercial iron	Intermediate in purity between Cast iron and Wrought iron
Hardness	Hard	Soft	Hard and soft
Malleability	Brittle	Malleable	Malleable and brittle
Appearance	Crystalline	Fibrous	Crystalline
Melting point	1200°C	1500°C.	1300° - 1400°C.
Tempering	Cannot be tempered	Can not be tempered	Can be tempered
Magnetisation	Cannot be permanently magnetised.	Can not be permanently magnetised	Can be permanently magnetised

The difference in properties of the different forms of iron is due to the presence of different proportions of other elements, combined and uncombined, in iron.

Uses : *Cast iron* is used for casting ornamental iron goods like railings as also for iron articles. It is also used for the manufacture of steel and wrought iron. *Steel* is used in the manufacture of railway lines, locomotives, joists, etc. ; in the manufacture of war implements, surgical instruments, cutlery, etc. It is also used in preparing artificial magnets, watch springs, etc. Wrought iron is used in the preparation of cores of electromagnets, piano wires and wires for binding flowers.

Herein a description of production of cast-iron from the oxide ores is described.

The ores generally employed for the extraction of iron are the oxides. These ores are first roasted in order to drive off water and carbon dioxide, to render the mass porous and to convert the ferrous oxide to ferric oxide. The oxide, thus obtained, is then reduced with coke and limestone in a blast furnace. The blast furnace is made of steel and lined inside with fire-bricks. It is from 50 to 80 ft. in height and is broadest

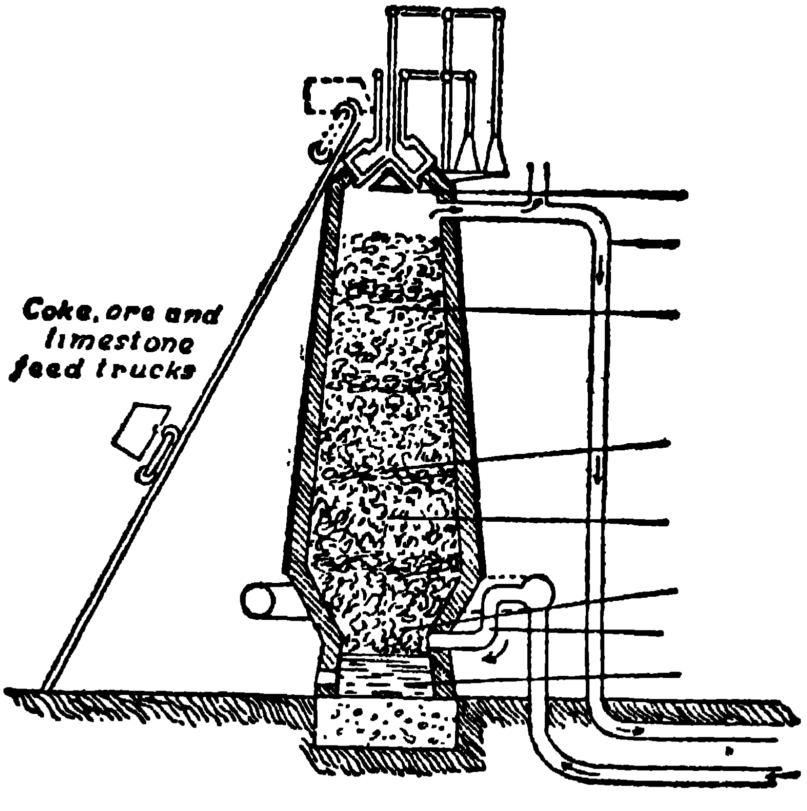


Fig. 109

at the middle. The top of the furnace is closed by a *cup-and-cone* arrangement. The calcined ore mixed with coke and limestone, is introduced into the furnace, by lowering the cone. A blast of heated air at a temp. of 700° – 800°C. is then introduced through the jets at the bottom, known as tuyeres, placed round the base of the furnace. The oxygen of the air combines with the carbon to form carbon monoxide which brings about the reduction of the iron oxide to iron.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

A portion of Fe_2O_3 that may escape reduction by CO is reduced by carbon itself. The spongy iron so obtained at a temp. of 1000°C. absorbs various impurities like carbon, sulphur, phosphorus and silicon from the ore, coke, etc. This impure iron melts and descends to the bottom of the furnace. Lime obtained by the decomposition of the limestone at the temperature of the furnace, combines with the siliceous impurities present in the ore forming a slag which flows down with the molten iron to the hearth. The slag, being lighter than the molten iron, floats on its surface, and thus prevents oxidation of the iron by the oxidising action of the blast.

$$CaCO_3 = CaO + CO_2$$
$$CaO + SiO_2 = CaSiO_3 \text{ (slag).}$$

As the slag reaches a certain height, it runs out through certain openings known as **slag-holes**; the iron is run off at suitable intervals and allowed to flow into moulds of sand. Iron, thus obtained, is known as **pig iron** or **cast iron.**

When metallic iron is placed in a solution of copper sulphate, metallic copper is thrown out of solution as a precipitate and iron passes into solution as ferrous sulphate.

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Q. 5. Alternative :

Mercury is known to form two varieties of compounds. Give examples. How would you distinguish between them? Describe the preparation and properties of one compound of each type.

Describe the action of nitric acid upon mercury, giving equations.

Ans. Mercury forms two series of compounds, *viz.*, mercurous and mercuric. Examples of mercurous compounds are mercurous chloride, Hg_2Cl_2, mercurous nitrate, $Hg_2(NO_3)_2$, mercurous sulphate, Hg_2SO_4 etc.

Examples of mercuric compounds are mercuric chloride, $HgCl_2$, mercuric nitrate, $Hg(NO_3)_2$, mercuric sulphate, $HgSO_4$ etc.

Soluble mercurous and mercuric compounds can be differentiated by adding

(1) Dil. HCl, when mercurous compounds will give a white ppt. of mercurous chloride but mercuric compounds will yield no ppt.

(2) NaOH solution, when mercurous compounds will give a grey ppt. of Hg_2O, whereas mercuric compounds will yield a yellow ppt. of HgO.

(3) NH_4OH, when mercurous compounds will give a black ppt., whereas mercuric compounds will yield a white ppt.

(4) KI solution, when mercurous compounds will yield a yellowish green ppt. of Hg_2I_2, whereas mercuric compounds will give a red ppt. of HgI_2, soluble in excess of KI solution yielding a colourless solution.

(5) H_2S, when mercurous compounds will give a black ppt. at once of HgS mixed with finely divided mercury, whereas mercuric compounds will at first give a white ppt. which gradually turns yellow, then brown and finally black (HgS only is pptd.)

N. B. Insoluble mercurous compounds like mercurous chloride is recognised by adding NH_4OH to it, when it turns immediately black.

One compound of mercurous mercury described here is mercurous chloride.

Mercurous chloride (*Calomel*), Hg_2Cl_2, is obtained as a curdy white precipitate when the solution of a soluble mercurous salt, say, of mercurous nitrate, is treated with HCl or with the solution of a chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 + 2NaNO_3.$$

This substance is manufactured by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel. Hg_2Cl_2 sublimes off and condenses as a white cake in the upper cooler part of the vessel. The sublimate is taken out and repeatedly boiled with water to free it completely from unchanged mercuric chloride, filtered and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Properties of mercurous chloride :—It is an amorphous white powder without any taste. It is insoluble in water and in dilute acids. It sublimes without decomposition when heated. It dissolves in aqua regia forming mercuric chloride. When treated with ammonia, it turns black due to the formation possibly of a mixture of finely divided mercury and amidomercuric chloride, NH_2HgCl.

One compound of mercuric mercury described here is mercuric chloride.

Mercuric chloride (*corrosive sublimate*), $HgCl_2$, is prepared by heating a mixture of mercuric sulphate and common salt in long-necked flat-bottomed flasks on a sand-bath,

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

A little MnO_2 is added to prevent reduction of $HgCl_2$ formed to calomel by organic matter. After the reaction is over, the flasks are cooled and these flasks are then broken and the cake of mercuric chloride is removed. It is then dissolved in water by heating and purified by recrystallisation from water solution.

Properties of mercuric chloride :—It is a white crystalline solid, soluble in water, but more soluble in organic solvents like ether and alcohol. It is extremely poisonous. Albumen (white of eggs) forms an insoluble compound with it, and so it is used as an antidote against suspected mecuric chloride poisoning. Stannous chloride readily reduces mercuric chloride, first into mercurous chloride and then into metallic mercury, excess of $SnCl_2$ being used.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

It produces a white precipitate, called ***infusible white precipitate*** (NH_2HgCl), with ammonia and it gives rise to a red precipitate of mercuric iodide with potassium iodide solution.

$$HgCl_2 + NH_3 = NH_2HgCl + HCl$$
$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

Hot and concentrated nitric acid dissolves mercury with the formation of mercuric nitrate ; but cold and dilute nitric acid reacts with excess of mercury, forming mercurous nitrate.

$$2Hg + 6HNO_3 \text{ (hot and conc.)} = 2Hg(NO_3)_2 + NO + NO_2 + 3H_2O.$$
$$6Hg + 8HNO_3 \text{ (cold and dilute)} = 3Hg_2(NO_3)_2 + 2NO + 4H_2O.$$

1955

FIRST PAPER

Q. 1. (*a*) *Giving chemical reactions and equations wherever necessary, explain the following :*

(*i*) *Solid dry quicklime, on being kept in air, becomes hot, gradually crumbles into powder and increases in weight.*

(*ii*) *A dry and fine mixture of carbon, sulphur and potassium nitrate burns with explosion.*

(*iii*) *Luminous flame of Bunsen burner deposits soot on the surface of a porcelain basin if exposed to it.*

(*b*) *State what happens when :*

(*i*) *Sulphur dioxide gas is passed, through sodium carbonate solution.*

(*ii*) *Dilute solutions of ammonium chloride and sodium nitrite are mixed together and gently warmed.*

Ans. (*a*) (*i*) Dry quicklime absorbs moisture from air and is thereby converted into slaked lime. So a chemical reaction occurs between calcium oxide, CaO, which is called quicklime, and water with the formation of calcium hydroxide, $Ca(OH)_2$, which is called slaked lime, with the evolution of heat.

$$CaO + H_2O = Ca(OH)_2.$$

This chemical transformation makes solid quicklime to crumble to powder. Then the slaked lime produced absorbs further carbon dioxide present in air with the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Calcium carbonate formation is also another cause of the powdery nature of the final product.

Now in the reactions stated above water and carbon dioxide are added to calcium oxide and hence the lump of quicklime increases in weight by exposure to air.

(*ii*) The mixture is essentially *gun powder*. When ignited, both carbon and sulphur aro oxidised by potassium nitrate with burning with evolution of carbon dioxide and sulphur dioxide as gas. The sudden deflagration of the mass due to quick oxidation is the cause of explosion.

$$4KNO_3 + 2S + 6C = 2K_2S + 6CO_2 + 2N_2.$$

(*iii*) Luminous flamo of Bunsen burner is produced by the incomplete combustion of the decompositon products of the hydrocarbons fed into the burner. So solid carbon particles are present in the luminous flame of the burner (in fact, the luminosity of the flame is due to the presence of solid carbon particles in it.)

$$C_2H_2 = 2C + H_2$$
$$2H_2 + O_2 = 2H_2O.$$

With acetylene the above reactions take place in the flame. When a cold porcelain basin is held in the luminous flame, these unburnt carbon particles are deposited as soot on the cold surface of the porcelain basin.

(*b*) (*i*) At first sodium sulphite is formed in solution with the evolution of carbon dioxide as gas.

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2.$$

On further passage of sulphur dioxide through the solution, sodium sulphite is converted into sodium bisulphite which also remains in solution.

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3.$$

(*ii*) When a mixed solution of ammonium chloride and sodium nitrite is gently warmed, ammonium nitrite is first formed by double decomposition and then nitrogen gas is evolved ; due to the decomposition of ammonium nitrate formed.

$$NH_4Cl + NaNO_2 = NaCl + NH_4NO_2$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

Q. 2. *Describe, with a neat sketch of the apparatus used, the laboratory method of preparation of sulphur dioxide. Give the tests which you would perform to demonstrate its principal properties. What is sulphurous acid ? How can you prepare it ?*

Ans. In the laboratory, sulphur dioxide is prepared in the following way :—Some copper turnings are taken in a flask fitted with a thistle funnel and a delivery tube. Concentrated H_2SO_4 is poured down the thistle funnel till the end of the funnel remains dipped under the surface of the acid. The flask is then placed on a piece of wire gauze and heated till the gas begins to be evolved. The source of heat is then removed and the gas is collected by the upward displacement of air. The gas is fairly dry and pure, but may be further dried by passing through a wash bottle containing concentrated sulphuric acid and collected over mercury.

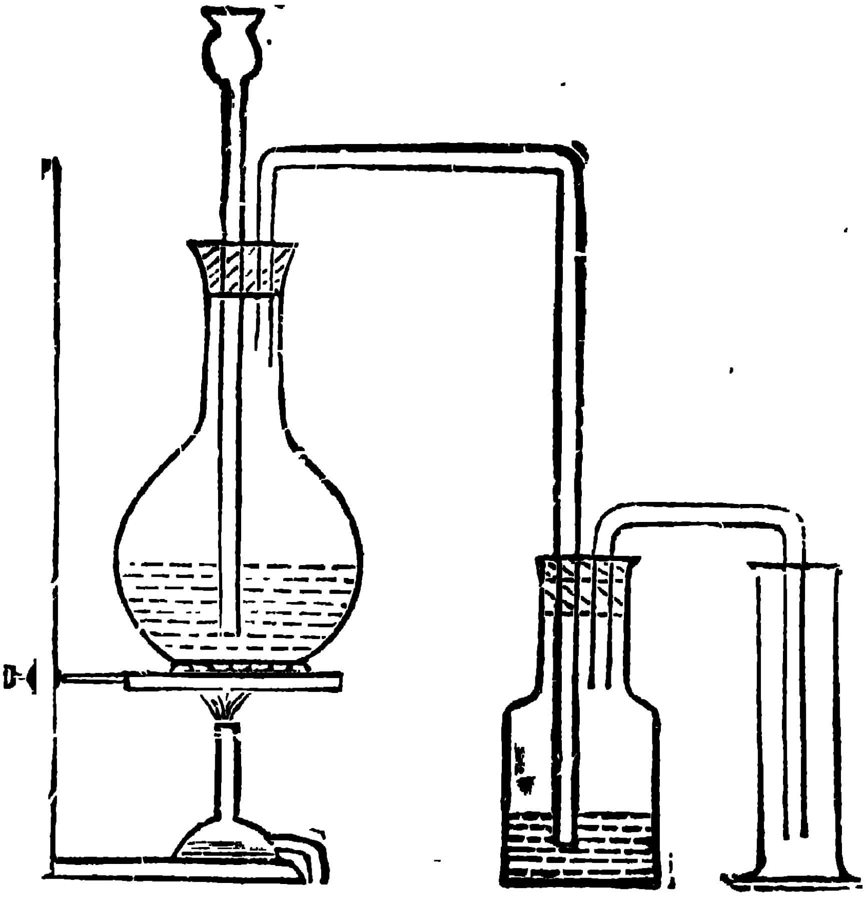


Fig. 110

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Properties :

(*i*) Sulphur dioxide neither burns nor ordinarily supports combustion.

A lighted candle is introduced into a jar of sulphur dioxide. The candle flame is extinguished and the gas does not burn.

(*ii*) Sulphur dioxide is readily soluble in water and the solution is acidic to litmus.

A flask is fitted with cork through which passes a glass tube. The flask is dried and then filled with sulphur dioxide gas by upward displacement of air. The cork with the glass tube is then fitted in. The flask is then inverted and the end of the glass tube is dipped into litmus solution contained in a beaker. The flask is then cooled, when coloured water is found to rise in the glass tube. As soon as a drop of water reaches the top of the glass tube, it dissolves the whole of sulphur dioxide present in the flask. Coloured water then rushes up and enters the flask in the form of a fountain. The violet blue colour of the litmus solution turns red inside the flask, showing the acid nature of the solution.

$$H_2O + SO_2 = \underset{\text{Sulphurous acid.}}{H_2SO_3.}$$

(*iii*) Sulphur dioxide is a powerful reducing agent.

Sulphur dioxide gas is passed through a yellow solution of ferric chloride. The solution turns colourless or light green due to the reduction of ferric chloride to ferrous chloride.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

(*iv*) Sulphur dioxide is a good bleaching agent.

Red flowers, moistened with water, are introduced into a jar of sulphur dioxide. The flowers are gradually decolorised.

(*v*) Sulphur dioxide behaves as an oxidising agent in certain cases.

Sulphur dioxide gas is passed into a solution of sulphuretted hydrogen. Sulphur is deposited from the oxidation of H_2S as also from the reduction of SO_2 by H_2S.

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

Sulphurous acid is an unstable dibasic acid, which is in a lower state of oxidation than sulphuric acid. It has not been isolated, but is produced only in aqueous solution.

It can be prepared by passing sulphur dioxide gas into water and it smells of sulphur dioxide.

$$H_2O + SO_2 = H_2SO_3.$$

On boiling all the sulphur dioxide is expelled from solution.

Q. 3. *Assuming that granulated zinc completely reacts with sulphuric acid, calculate the amount of the former (i.e., granulated zinc) which would give 1000 c.c. of dry Hydrogen at 30°C.,* and *754 mm. pressure.*

$$[Zn = 65{\cdot}5,\ H = 1,\ S = 32,\ O = 16].$$

Ans. Let V c.c. be the volume of dry Hydrogen evolved at N.T.P., *i.e.*, at 0°C. and 760 m.m. pressure,

Then, by Boyle's Law and Charles' Law, we have

$$\frac{1000 \times 754}{273 + 30} = \frac{V \times 760}{273 + 0}$$

$$\therefore\ V = \frac{1000 \times 754 \times 273}{760 \times 303} \text{ c.c.}$$

$$= 894{\cdot}1 \text{ c.c.}$$

Now, from the equation

$$\begin{array}{l} Zn + H_2SO_4 = ZnSO_4 + H_2 \\ 65{\cdot}5 \qquad\qquad\qquad\qquad\quad 2 \end{array}$$

We know that 65·5 grams of zinc, when reacted upon by sulphuric acid, gives rise to 2 grams of hydrogen. But 2 is the molecular weight of Hydrogen and so the Hydrogen evolved occupies 22·4 litres at N.T.P. since molecular weight of any gas, expressed in grams, occupies 22·4 litres at N.T.P.

Hence in order to get 22·4 × 1000 or 22400 c.c. of Hydrogen at N.T.P., we require 65·5 grams of zinc,

Therefore 894·1 c.c. of Hydrogen at N.T.P. can be obtained from the use of $\frac{65{\cdot}5}{22400} \times 894{\cdot}1$ grams or 2·614 grams of zinc.

Q. 4. *Describe the preparation of the following :—*

(*a*) *Ferrous sulphate from waste liquor of Kipp's apparatus.*

(*b*) *Anhydrous hydroflouric acid, starting from Calcium fluoride.*

(*c*) *Soda-ash from sodium bicarbonate. State their uses.*

Ans. (*a*) The waste liquor collecting at the bottom of Kipp's apparatus in which H_2S is generated by the action of H_2SO_4 on FeS contains $FeSO_4$ solution, dissolved H_2S and other impurities. It is taken out in a beaker, filtered into a wide porcelain basin and evaporated to crystallisation ; on cooling pale green crystals of hydrated ferrous sulphate, $FeSO_4$, $7H_2O$ (known as green vitriol) separate out. These are filtered, washed with a little cold water in order to free it from adhering mother liquor and then dried.

Uses.—It is used in the preparation of writing ink ; in the manufacture of jeweller's rouge ; in the dyeing industry and in medicine.

(*b*) Powdered calcium fluoride is first mixed with conc. H_2SO_4 and the mixture placed in a lead retort which is heated gently on a sand-bath. Hydrofluoric acid vapour is given off, which is absorbed in water contained in lead bottles. By this means 40% solution of HF is obtained.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The aqueous solution of HF thus obtained is divided into two parts. One part is neutralised with K_2CO_3 and to the neutralised solution the other part of the acid is added. The mixed solution is then evaporated in a platinum dish to crystallisation. On cooling, crystals of potassium hydrogen fluoride,

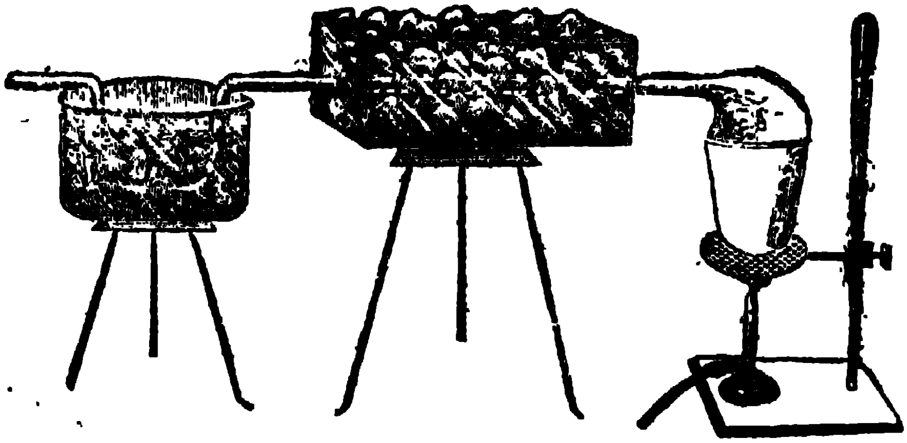


Fig. 111

KF, HF, known as Fremy's salt, separate out. These crystals are collected and thoroughly dried. Perfectly dry potassium hydrogen fluoride is next taken in a platinum retort, connected to a platinum U-tube by means of a long platinum tube. The long platinum tube as also the platinum U-tube are kept immersed in freezing mixture of ice and salt. The platinum retort is then heated, when KHF_2 first melts and then decomposes, giving off HF as vapour, which passes on and condense to a liquid in the platinum U-tube.

$$KHF_2 = KF + HF.$$

The liquid HF is taken out in a dry beaker and two platinum wires carrying electric current by joining them to the two poles of a battery are dipped into the liquid. Any moisture present in the acid is removed by decomposition into hydrogen and oxygen, which are evolved away as gas. As soon as the acid becomes perfectly anhydrous, the flow of current stops. The wires are then removed and perfectly anhydrous hydrofluoric acid is obtained.

Uses.—Hydrofluoric acid is used for etching designs on glass. On account of its sterilising properties, it is used for sterilising casks of wines as also for destroying wild yeast in the brewing industry. It is also employed for removing silica from iron castings and as an analytical reagent in the laboratory.

(*c*) When sodium bicarbonate is heated, soda-ash is produced.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Uses.—Soda-ash is used in the manufacture of glass and of caustic soda ; as a detergent (*i.e.*, for washing dirty clothes) ; for removing permanent hardness in water and as a reagent in the laboratory.

Q. 5. *How is distilled water prepared ? Give a sketch of the apparatus used ? How would you proceed to test its purity ?*

How can you distinguish it from ordinary drinking water ? Explain why in chemical laboratory solutions are always prepared with distilled water.

Ans. The process of distillation is carried out in the apparatus arranged as shown in the figure (see Fig. 112). Filtered water is taken in the distilling flask. The side tube of the distilling flask is introduced through a cork into Liebig's condenser as shown in the figure. Cold water enters the jacket by the lower side-tube and after circulating round the narrow inner tube, and getting heated in contact with steam passing through the inner tube leaves by the upper side-tube. The arrangement for this cold water circulation through the jacket is shown in the adjoining figure. A clean flask (called a receiver) is placed at the other end of the condenser for collecting the condensed water. A thermometer is introduced into the distilling flask through a cork fitted to its neck. The bulb of the thermometer is placed slightly below and nearly opposite to the side-tube of the distilling flask as shown in the figure. The distilling flask containing water is then heated over a piece of wire gauze by means of a Bunsen flame, till the liquid in the flask boils. The vapour of water, given off during boiling, passes through the inner tube of the Liebig's condenser and condenses back into liquid water there due to the cooling action of cold water circulating through the jacket and collects inside the receiver after trickling down the inner tube. The water collecting in the receiver is called the distillate. The thermometer indicates the boiling point of water, being the temperature of steam and so indicates the purity of the water vapour.

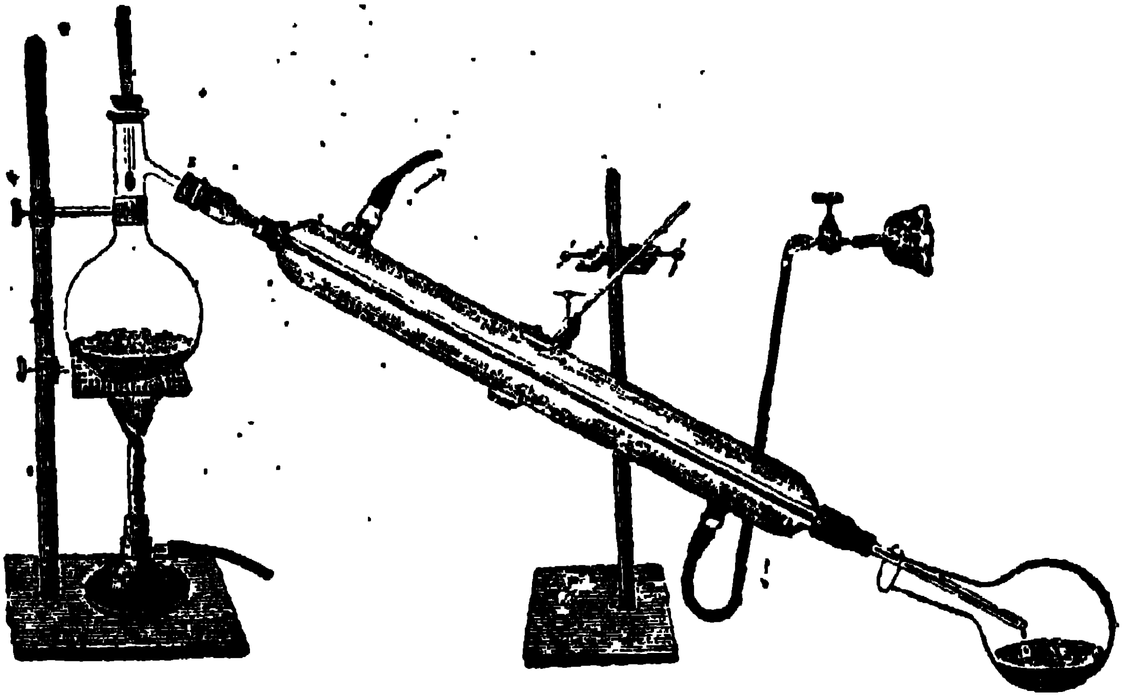


Fig. 112

The purity of water obtained by distillation can be tested by adding (1) silver nitrate solution, when there will be no opalescence due to precipitation of insoluble silver chloride which is produced with ordinary water due to the presence of dissolved chloride in it ; (2) barium chloride solution, when there will be no cloudiness due to precipitation of insoluble barium sulphate which is formed with ordinary water on account of the presence of dissolved sulphate in it ; (3) Nessler's solution (an alkaline solution of mercuric iodide in potassium iodide), when no coloration will be produced, showing the absence of ammonium compounds in it ; ordinary water produces yellow coloration with the reagent mentioned on account of the presence of ammonium compounds derived from nitrogenous organic compounds with which it comes in contact during it's flow and which it dissolves on account of its solvent action ; (4) lime water when no turbidity is produced showing the absence of dissolved CO_2, bicarbonates of Ca and Mg and soluble carbonates. The physical tests may also be applied to show the purity of distilled water, *viz.*, it is colourless, neutral to litmus, freezes at 0°C., and boils at 100°C., under 760 mm. pressure.

Ordinary drinking water contains dissolved air and also dissolved salts and the reagents mentioned above will show the presence of chloride, sulphate, ammonium salts and carbonates and bicarbonates to be present in it. Distilled water is insipid to taste whereas drinking water possesses a pleasant taste due to the presence of dissolved salts (in traces) mentioned and dissolved air in it. In Chemical laboratory distilled water is used for preparing solutions of reagents on account of the fact that foreign materials should be absent from their solutions in order that desired reactions can be correctly observed and be not vitiated by the presence of foreign matter. Besides in some cases due to double decomposition occurring between dissolved materials in ordinary water and the reagent, clear solution cannot be obtained, for example, silver nitrate does not give a clear solution with ordinary tap water due to the presence of chloride in that water. Hence the necessity of using distilled water in preparing the solution of silver nitrate in the laboratory. Such is the case with other reagents also.

Q. 6. *A weighed quantity of ammonium chloride was boiled with an excess of strong caustic soda solution and the liberated gas was absorbed by 100 c.c. of a solution containing 4·9 gm. of*

H_2SO_4 ; part of the acid was thus neutralised and the excess acid could be neutralised by 50 c.c. of sodium carbonate solution containing 2·26 gm. of Na_2CO_3. Calculate the amount of ammonium chloride originally taken.

[N = 14, H = 1, Cl = 35·5, Na = 23, C = 12, S = 32, O = 16.]

Ans. From the equation

$$\underset{98}{H_2SO_4} + \underset{106}{Na_2CO_3} = Na_2SO_4 + CO_2 + H_2O$$

we know that 106 grams of Na_2CO_3 react with 98 grams of H_2SO_4. Since the remaining H_2SO_4 after reaction with ammonia evolved reacts with 2·65 grams of Na_2CO_3, therefore the amount of H_2SO_4 left over

$$= \frac{98}{\underset{2}{\cancel{106}}} \times \overset{\cdot 05}{\cancel{2\cdot65}} \text{ grams, or } \frac{4\cdot90}{2} \text{ gms. or } 2\cdot45 \text{ gms.}$$

Therefore H_2SO_4 used up by ammonia evolved = (4·9 − 2·45) or 2·45 grams.

Now from the equations

$$\underset{53\cdot5}{NH_4Cl} + NaOH = NaCl + \underset{17}{NH_3} + H_2O$$

and

$$\underset{2\times17}{2NH_3} + \underset{98}{H_2SO_4} = (NH_4)_2SO_4$$

We find that 98 grams of H_2SO_4 can react with 2 × 17 grams of NH_3 which can be obtained from 2 × 53·5 gms. of ammonium chloride.

Therefore 98 grams of $H_2SO_4 \equiv 2 \times 53\cdot5$ grams of NH_4Cl.

$$\text{Hence } 2\cdot45 \text{ grams of } H_2SO_4 \equiv \frac{\cancel{2}\times 53\cdot5}{\underset{\underset{\cdot20}{\cancel{49}}}{\cancel{98}}} \times \cancel{2\cdot45} \text{ grams of } NH_4Cl. \equiv 2\cdot675 \text{ grams of } NH_4Cl.$$

Therefore amount of ammonium chloride originally taken = 2·675 grams.

N. B. The sum is on acidimetry and alkalimetry, which is included in the revised syllabus circulated in Paper II. Yet it is set in Paper I due to oversight on the part of the Paper-setter. Hence it is worked out here on the weight basis. Evidently, both H_2SO_4 solution and Na_2CO_3 solution are Normal in character. Therefore 50 c.c. of (N) H_2SO_4 are used up to neutralise ammonia evolved from ammonium chloride. From the equations written above, it is evident that

$$1000 \text{ c. c. (N) } H_2SO_4 \equiv 53{\cdot}5 \text{ grams } NH_4Cl.$$

$$\therefore \quad 50 \text{ c.c. (N)} H_2SO_4 \equiv \frac{53{\cdot}5}{1000} \times 50 \text{ ,, ,, ,,}$$

$$= 2{\cdot}675 \text{ grams } NH_4Cl.$$

Q. 7. *How can you prove that the molecular formula of sulphuretted hydrogen is* H_2S *?*

Ans. A thumb-tube is filled with mercury completely and inverted over mercury in a trough. A few c.c. of sulphuretted hydrogen is introduced into the tube. The volume is carefully marked by means of a rubber ring. A piece of metallic tin is introduced into the horizontal part of the tube and it is heated by a burner. Tin combines with the sulphur of sulphuretted hydrogen forming tin sulphide and liberating hydrogen. After allowing the tube to cool to the ordinary temperature, the mercury is found to stand at the same level as before. The residual gas can be proved to be hydrogen. Hence the volume of hydrogen liberted is equal to the volume of sulphuretted hydrogen decomposed, or sulphuretted hydrogen contains its own volume of hydrogen.

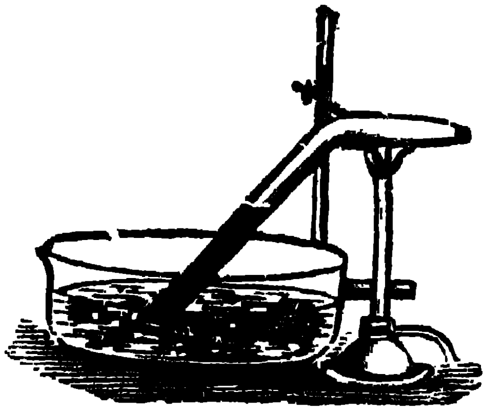


Fig. 113

From the result given, it is inferred that hydrogen sulphide contains its own volume of hydrogen. Let "n" be the number of molecules present in 1 vol. of hydrogen sulphide.

Then, since 1 vol. of hydrogen sulphide contains 1 vol. of hydrogen, therefore "n" molecules of hydrogen sulphide contain "n" molecules of hydrogen. (Avogadro's hypothesis). Hence, 1 molecule of hydrogen sulphide contains 1 molecule, or 2 atoms of hydrogen, since hydrogen molecule is diatomic. (Deduction from Avogadro's hypothesis). Thus the formula for hydrogen sulphide is H_2S_x, where x is an integer. Now since the density of hydrogen sulphide is given to be 17, its molecular weight is $2 \times 17 = 34$ (Deduction from Avogadro's hypothesis).

Therefore

$$2 \times 1 + 32 \times x = 34$$
$$\text{or} \quad 32 \times x = 32$$
$$\therefore x = 1$$

Thus, the formula for hydrogen sulphide is H_2S.

Q. 8. *Write what you know about*

(*a*) *Law of Multiple proportions,*

(*b*) *Dissociation,*

(*c*) *Catalytic agent.*

Ans. (*a*) Law of multiple proportions is stated as follows :—

When one element combines with another element to form two or more different compounds, the weights of one of the elements combining with a constant weight of the other, bear a simple ratio to one another.

The expression *simple ratio* means that ratio can be expressed by simple whole numbers.

Examples. (1) There are two oxides of hydrogen known, viz., water and hydrogen peroxide.

In water, 1 part by weight of hydrogen is found to have combined with 8 parts by weight of oxygen. In hydrogen peroxide, 1 part by weight of hydrogen is chemically combined with 16 parts by weight of oxygen. Thus, the weights of oxygen, viz. 8 and 16, which unite in these cases, with the same weight of hydrogen, viz. 1, bear to each other the ratio 8 : 16 or 1 : 2, which is a simple ratio.

(2) Similarly, carbon and oxygen combine together to give two oxides, viz. carbon monoxide and carbon dioxide.

In **Carbon monoxide**

12 parts by weight of carbon has combined with 16 parts by weight of oxygen.

In **Carbon dioxide**

12 parts by weight of carbon has combined with 32 parts by weight of oxygen.

Therefore, the weights of oxygen, viz. 16 and 32, which combine with a constant weight of carbon, viz. 12, are in the ratio of 16 : 32, *i.e.*, as 1 : 2, which is a simple ratio.

The law of Multiple proportions can be deduced from Dalton's Atomic theory.

The fundamental postulates of Dalton's Atomic theory are :

(*i*) Matter is composed of *minute indivisible* particles called atoms, which can neither be created nor destroyed by any chemical process.

(*ii*) Atoms of the same element are similar in properties in all respects and are equal in weight.

(*iii*) Atoms of different elements have different properties and different weights.

(*iv*) Chemical combination between two or more elements takes place by the union or juxtaposition of the atoms of those elements in simple numerical proportions, viz. 1 : 1, 1 : 2, 2 : 1, or 2 : 3, etc.

(*v*) The combining weights of the elements represent the combining weights of the atoms of different elements concerned.

In explaining the law of multiple proportions from the postulates of Dalton's atomic theory, let us assume that two elements A and B combine together to give more than two different compounds. Let us also assume that the simplest compound formed from A and B contains 1 atom of A and 1 atom of B, so that its formula is AB. Since atoms are indivisible and compounds are formed by the union of atoms in simple numerical proportions, 1 or more atoms of A will now combine with 2 or more atoms of B to give the other compounds of **A** and B. Let the formula for *another* compound of A and B be AB_2 and yet a third compound of A and B is found whose formula is A_2B_3. Let us assume that the atomic weights of A and B be m and n respectively. Then we find that

(*i*) In the first compound AB,

n parts by weight of B have combined with m parts by weight of A.

(*ii*) In the second compound AB_2,

$2n$ parts by weight of B have combined with m parts by weight of A,

i.e., n parts by weight of B have combined with $\frac{m}{2}$ part by weight of A.

(*iii*) In the compound A_2B_3,

$3n$ parts by weight of B have combined with $2\,m$ parts by weight of A.

i.e., n parts by weight of B have combined with $\frac{2m}{3}$ part by weight of A.

Therefore, the weights of A which combine with a constant weight of B, viz. n, are as $m : \frac{m}{2} : \frac{2m}{3}$, or as $1 : \frac{1}{2} : \frac{2}{3}$, or as $6 : 3 : 4$, which is a simple ratio. Hence it is seen that the law of multiple proportions follows as a necessary corollary from Dalton's Atomic theory.

(*b*) When a chemical compound decomposes under the influence of heat and the products are capable of recombining to form the original compound under exactly the same condition, the process is said to be one of dissociation.

Thus, when ammonium chloride, NH_4Cl, is heated in a closed vessel, it breaks up into NH_3 and HCl but NH_3 and HCl recombine to form NH_4Cl under similar conditions until a dynamic equilibrium is set up.

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

Similarly, in case of PCl_5,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

or, of I_2, $I_2 \rightleftarrows I + I$

This phenomenon is also called *thermal dissociation.*

There is another type of dissociation called *electrolytic dissociation.*

When acids, bases and salts are dissolved in water, they are said to break down into electrically charged particles called ions. This breaking up into electrically charged particles of the above class of substances on being dissolved in water is known as *ionisation*. This is a reversible phenomenon.

Thus, nitric acid in water solution is stated to break up as follows :—

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

Also $$KOH \rightleftharpoons K^+ + OH^-$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^-$$

The breaking down into ions and recombination of ions to form undissociated compound go on simultaneously until an equilibrium condition is set up, but water being removed the unionised compound is got back. This phenomenon is also called *electrolytic dissociation*.

(*c*) *Catalytic agent*—When a substance, by its mere presence, in small quantities, influences the rate of a chemical reaction, without itself undergoing any change in mass and in chemical composition, it is called a catalytic agent.

Thus, in the preparation of oxygen from $KClO_3$, MnO_2 is added to hasten the rate of decomposition of $KClO_3$ by heat. Here, MnO_2 acts as a catalytic agent because it does not undergo any alteration in mass or in chemical composition during the reaction as shown by experiments after the decomposition of $KClO_3$ is complete by dissolving out the KCl formed by water. Catalytic agents act mostly as contact agents, *e.g.*, platinised asbestos used as a catalytic agent in the conversion of a mixture of SO_2 and O_2 into SO_3 at 450°C. In some cases catalytic agents are stated to take part in the reaction and then to be regenerated.

Second Paper

Q. 1. *How is methane usually prepared and collected ? What happens when it is (a) led over red-hot cupric oxide, (b) burnt in an atmosphere of chlorine ? How would you distinguish between methane and a mixture of ethylene with twice its volume of hydrogen.*

Ans. Methane is usually prepared by heating fused sodium acetate with soda lime in a hard glass tube.

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

The gas is collected by displacement of water.

(*a*) When methane is passed over red-hot cupric oxide, cupric oxide is reduced to metallic copper, and carbon dioxide and water are produced from the oxidation of methane.

$$4CuO + CH_4 = 4Cu + CO_2 + 2H_2O.$$

(*b*) When methane is burnt in an atmosphere of chlorine, carbon separates in the form of soot and fumes of hydrogen chloride are evolved.

$$CH_4 + 2Cl_2 = C + 4HCl.$$

Methane and a mixture of ethylene with twice its volume of hydrogen can be distinguished by the following tests :—

(*a*) When a lighted taper is applied to both of them, methane burns with a scarcely-visible blue flame, whereas the mixture of ethylene and hydrogen will burn with a luminous flame.

(*b*) Bromine-water is added to jars containing methane and mixture of ethylene and hydrogen. Methane does not react with bromine, but in the mixture bromine-water is decolorised.

(*c*) Two jars, one containing methane and the other containing the mixture of ethylene and hydrogen, are inverted over conc. H_2SO_4 after a few c.c. of fuming sulphuric acid are added to the jars and the jars shaken thoroughly. Concentrated H_2SO_4 rises in the jar in which the mixture of ethylene and hydrogen is present, since ethylene is absorbed by fuming sulphuric acid, but methane is not absorbed. If the volume of the gas in the jar containing the mixture of 1 vol. of ethylene and 2 vols. of hydrogen be divided into three equal parts by two rubber bands, then conc. H_2SO_4 will rise nearly upto the first rubber band. On making the level of sulphuric acid inside and outside the same jar, the sulphuric acid level will stand exactly at the first rubber band from the bottom. Thus out of 3 vols., 2 vols, of gas are left unabsorbed and this unabsorbed gas can be proved by usual tests to be hydrogen.

Q. 2. *Explain with equations what happens when :—*

(*a*) *concentrated sulphuric acid is heated with sodium iodide ;*

(*b*) *red phosphorus is boiled with nitric acid :*
(*c*) *burning magnesium is put into a jar of carbon dioxide ;*
(*d*) *ammonium nitrate is heated ;*
(*e*) *hydrogen peroxide reacts with ozone.*

Ans. (*a*) When concentrated sulphuric acid is heated with sodium iodide, hydriodic acid that is first liberated from sodium iodide reduces sulphuric acid first to sulphur dioxide, then to sulphur and finally to sulphuretted hydrogen ; itself being oxidised to iodine which is evolved as violet vapour.

$$NaI + H_2SO_4 = NaHSO_4 + HI$$
$$H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O$$
$$H_2SO_4 + 6HI = S + 3I_2 + 4H_2O$$
$$H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2.$$

(*b*) Phosphorus is oxidised to phosphoric acid and nitric acid is reduced to oxides of nitrogen.

$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

(*c*) Magnesium continues to burn and is oxidised by oxygen of carbon dioxide to magnesium oxide and carbon separates in the form of soot.

$$2Mg + CO_2 = 2MgO + C.$$

(*d*) Ammonium nitrate decomposes with evolution of nitrous oxide as gas and water as steam.

$$NH_4NO_3 = N_2O + 2H_2O.$$

(*e*) Oxygen is evolved, mutual reduction of ozone and hydrogen peroxide taking place,

$$O_3 + H_2O_2 = H_2O + 2O_2.$$

Two atoms of loosely bound oxygen, one each from O_3 and H_2O_2, are set free and combine to form a molecule of oxygen.

Q. 2. Alternative.

Describe the preparation and uses of the following :—
(*a*) *potassium chlorate ;*
(*b*) *bleaching powder ;*
(*c*) *borax ;*
(*d*) *calomel ;*
(*e*) *anhydrous aluminium chloride.*

Ans. (*a*) *Potassium chlorate*—Potassium chlorate is now-a-days prepared on an industrial scale by the electrolysis of an aqueous solution of potassium chloride, KCl, at 80°—90°C., the cathode and anode being kept in the same compartment.

The apparatus consists of a lead-lined wooden vessel provided with mechanical stirrers, in which a conc. solution of KCl containing a little amount of HCl is taken. The anode is made of platinum-iridium alloy, while the cathode is of iron or graphite. A little quantity of $K_2Cr_2O_7$ is added to the solution in order to prevent the cathodic reduction of $KClO_3$ produced. Electric current is passed in, when KCl is decomposed. Potassium, liberated at the cathode, reacts with water of the solution, giving KOH and evolving H_2 which escapes as gas, Cl_2 is liberated at the anode. The temperature of the solution rises spontaneously which is maintained at about 80—90°C, Chlorine, liberated at the anode, now reacts with hot and conc. KOH sol., giving $KClO_3$ and KCl. $6KOH+3Cl_2=KClO_3+5KCl+3H_2O$. The solution is run out and crystallised when $KClO_3$ crystallises out and the mother liquor containing KCl used again.

Uses of potassium chlorate—$KClO_3$ is used in match industry, in pyrotechny, as a germicide and for the preparation of oxygen and potassium perchlorate.

(*b*) *Bleaching powder*—Dry slaked lime, $Ca(OH)_2$, is spread on the floor of a lead chamber, provided with glass door and windows and a fan arrangement for dusting in lime. Chlorine, free from CO_2 and HCl, is led in by a pipe near the top. The temperature is not allowed to rise above 40°C and the mass is left in that condition for about 24 hours. In the meantime lime is turned over with wooden rakes from time to time to expose fresh surface to the action of the gas. When the absorption of chlorine is complete, some lime is sprayed into the chamber with the help of the fan arrangement to get rid of the excess of chlorine. Bleaching powder is then removed by workmen and put into barrels.

$$Ca(OH)_2+Cl_2=Ca(OCl)Cl+H_2O.$$

Uses.—Bleaching powder is used as a bleaching agent and as a disinfectant.

(*c*) *Borax*, $Na_2B_4O_7, 10H_2O$.

Preparation—Borax is now-a-days exclusively prepared from naturally occurring calcium borates. Powdered *colemanite*,

$Ca_2B_6O_{11}$, is boiled with Na_2CO_3 solution when insoluble $CaCO_3$ precipitates out. It is filtered and the filtrate evaporated to crystallisation and crystals separated by filtration.

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

The mother liquor is afterwards treated with CO_2 whereby further quantity of borax can be obtained from it by concentration and crystallisation.

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

Uses.—Borax is used (i) in the manufacture of glass, enamels, glazes, soaps, etc. (ii) in medicine, (iii) in laundry, (iv) as a flux and (v) in soldering.

(*d*) *Mercurous chloride* (*calomel*), Hg_2Cl_2, is obtained as a curdy white precipitate when the solution of a soluble mercurous salt is treated with HCl or with the solution of a chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 + 2NaNO_3.$$

This substance is manufactured by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel. Hg_2Cl_2 sublimes off and condenses as a white cake in the upper part of the vessel. The sublimate is taken out and repeatedly boiled with water to free it completely from unchanged mercuric chloride, filtered and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Use of calomel.—Calomel or mercurous chloride is used in medicine as a purgative.

(*e*) *Anhydrous aluminium chloride* :—When chlorine is passed over a mixture of aluminium oxide and coke in a hard glass tube, anhydrous aluminium chloride is formed and volatilised. By condensing the vapour in a dry flask closed with a cork and passing the exit tube from the hard glass tube of reaction through the cork into the flask, an exit tube being also fitted through the cork fixed to the mouth of the flask,

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

Uses.—Anhydrous aluminium chloride is used in the synthesis of organic compounds and in the petroleum industry.

Q. 3. *What are the principal ores of copper? Describe any* one *process for the extraction of copper from its ores. Write equations. State the uses of copper.*

Ans. *Names and compositions of principal ores of copper* :

Ruby ore—Cu_2O
Copper glance—Cu_2S
Covellite or indigo copper—CuS
Copper Pyrites—Cu_2S, Fe_2S_3 or $CuFeS_2$
Purple copper ore—$3Cu_2S$, Fe_2S_3 or Cu_3FeS_3
Malachite—$CuCO_3$, $Cu(OH)_2$
Azurite—$2CuCO_3$, $Cu(OH)_2$

Extraction of copper from its ores.—The method of extraction of copper depends on the nature of the ore. Copper pyrites is most frequently used, but *the oxide or the carbonate ore of copper* can also be utilised for the purpose. In such cases the ore is first subjected to calcination, whereby oxide of copper is formed.

$$CuCO_3.Cu(OH)_2 = 2CuO + CO_2 + H_2O$$

The oxide of copper is then mixed with anthracite or coke and a little sand (sand being added to act as a flux), and the mixture is heated strongly in a *blast furnace* whereby the oxide is reduced to the metal.

$$Cu_2O + C = 2Cu + CO$$
$$CuO + C = Cu + CO$$
$$CuO + CO = Cu + CO_2$$

The flux combines with the gangue and forms a slag. The molten slag is run off and copper produced is taken out.

From copper pyrites.—Copper is extracted by a thermal process by the following operation :—

At first the ore is concentrated either by gravity separation or by Floatation process. For this purpose the ore is first crushed and finely powdered. The powdered ore is next churned with water containing a little pine oil and lime, by blowing air through it. By this operation a froth is produced which carries up along with it the particles of Cu-ore, leaving sand and other impurities behind. The froth is collected by skimming and allowed to settle.

The concentrated ore is next roasted in a multiple hearth furnace, whereby excess of sulphur present is burnt out to SO_2

and the metals, viz., Fe present in pyrites and Cu are partially oxidised.

$$Cu_2S,\ Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S,\ Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$

this last reaction occurring only to a very small extent.

(3) The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime: and the mixture heated in a water-jacketed blast furnace when the little quantity of Cu_2O formed in the previous operation reacts with the unchanged iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced during roasting operation reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained consisting of cuprous and ferrous sulphide is known as *matte.*

(4) The molten *matte,* mixed with a little sand, is then directly run into a converter of the Bessemer type, but with this difference that the air-ports are situated a little above the bottom level. A blast of air is next introduced through the air-ports. Iron is first oxidised to ferrous oxide, FeO, which combines with the silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued, whereby Cu_2S is partially oxidised to Cu_2O. When two-thirds of the matte is thus oxidised Cu_2O reacts with unchanged Cu_2S, giving, rise to metallic copper and sulphur dioxide. The slag is removed, the blast is stopped and the converter tilted to pour off molten copper. This copper, on cooling, is found to have a blistered appearance due to escape of sulphur dioxide and is known as "*blistered copper*".

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

(5) Blistered copper is now-a-days *refined* by an electrolytic method.

Thick blocks are made from blistered copper and are suspended from a metal rod into a bath of copper sulphate solution, acidified with 15% of sulphuric acid, and contained in a lead-lined wooden vat. The metal rod carrying these thick slabs is connected to the positive pole of a battery and is thus made the anodes. Thin plates of pure copper are suspended in the same bath from another metal rod which in its turn is connected to the negative pole of the same battery and is thus made the cathodes. These thin plates are so arranged that they are alternately inserted between the thick blocks. On passing electric current through the bath of copper sulphate, copper from the thick slabs passes into solution as cupric ions and pure copper is deposited from the bath on the pure copper sheets serving as cathodes. Impurities present either pass into solution or are deposited at the bottom of the bath near the anodes as anode mud. Copper, thus obtained as a deposit on the cathode, is 99·99 per cent. pure.

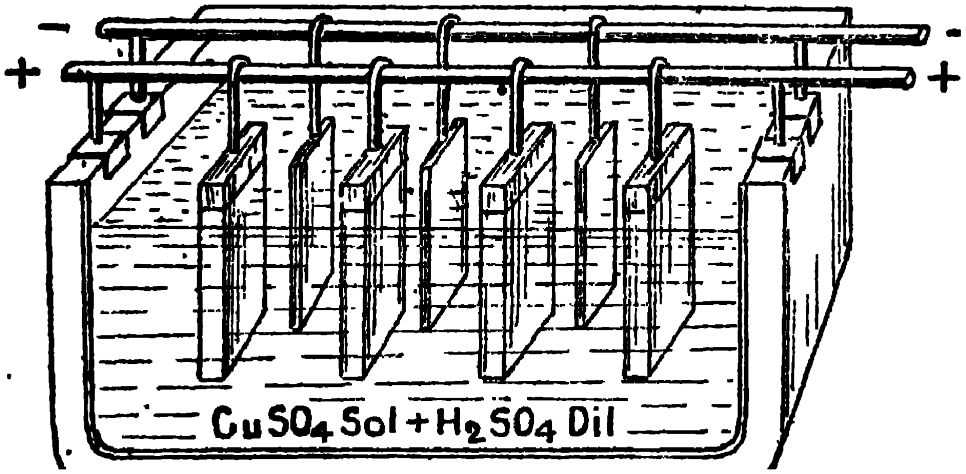


Fig. 114

Uses of Copper : Copper is used largely in electric industry—in electrotyping, for cables and wires for conveying electric current ; in the preparation of household utensils, for coinage and for the preparation of important alloys, like brass, bronze, German silver, etc.

Q. 3. Alternative.

Give the names and formulae of the oxides of lead and state their preparation and uses.

How is lead extracted from galena ?

Ans. Four oxides of lead are important :—

(1) *Lead monoxide*, commercially known as *massicot* and *litharge*, PbO.

(2) *Lead sesquioxide*, Pb_2O_3.

(3) *Red lead*, called also *minium*, Pb_3O_4.

(3) *Lead dioxide* or *lead peroxide*, PbO_2.

(1) Massicot is a yellow powder, obtained by heating lead, lead nitrate, or lead carbonate in air. It is obtained as a by-product during the cupellation operation performed on argentiferous lead.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

When massicot is heated, it melts and the molten mass on cooling forms the buff-coloured crystalline variety, called litharge.

Uses.—It is used in making flint glass, in glazing stoneware and earthenware articles ; in the preparation of lead salts and in making paints and varnishes.

(2) Lead sesquioxide, Pb_2O_3, is prepared by adding sodium hypochlorite or H_2O_2 to a cold solution of lead monoxide in NaOH solution.

$2Pb + 3NaOCl = Pb_2O_3 + 3NaCl$. It has practically no use.

(3) Red lead is manufactured from lead. First metallic lead is heated in a current of air, when it is converted into PbO. This PbO is removed from the furnace and hammered, when any particle of unoxidised lead is flattened out. Powdery PbO is then removed by sieving. Finely powdered PbO is then heated in a barrel-shaped vessel, open at both ends, in excess of air at 400°C. for 48 hours, whereby red lead is formed. It is removed, washed and dried.

$$6Pb + 3O_2 = 6PbO$$
$$6PbO + O_2 = 2Pb_3O_4$$

Uses.—It is used as a paint along with linseed oil. It is also employed in the manufacture of flint glass and of matches.

(4) Lead dioxide is prepared by treating red lead with conc. HNO_3 in the cold. Solution of lead nitrate is formed along with insoluble lead dioxide. Water is added to dilute the solution

and then the mixture is filtered. The residue of PbO_2 is washed and dried.

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Uses.—Lead dioxide is used in storage cells, in the manufacture of matches and as an oxidising agent in the laboratory.

Lead is extracted from galena now-a-days by the carbon-reduction process carried out in a blast furnace.

(*i*) The ore galena, PbS, is first crushed into fine powder. The powdered ore is next mixed with water, a little pine oil, and a frothing agent like xanthate. Air is then blown through it, whereby froth is produced in large quantities. Galena is preferentially wetted by oil and rises up with the froth. The worthless impuritirs like silica get wetted by water and sink down. The froth is skimmed off and collected. The ore is thus concentrated.

(*ii*) The concentrated ore is next sintered in a pot, mounted on trunnions and provided with a hood for collecting fumes. The powdered ore, after drying, is mixed with coke and lime and fed into the pot which has a fire on a grating beneath. A slow blast of air is passed through the bottom. Sulphur present in galena burns out to SO_2 which escapes as gas and lead oxide is produced. The ore by this operation agglomerates into a compact porous cake of mostly PbO.

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

(*iii*) The sintered mass is broken up into lumps of proper size and fed into a small blast furnace which is water-jacketed upto the top, together with coke, limestone and iron ore through a charging pipe in such a way that the charge settles just beneath the waste-gas outlet. A blast of air is admitted through tuyeres set near the bottom. At first PbO is reduced by carbon present in the charge.

$$PbO + C = Pb + CO.$$

The carbon monoxide formed then reduces PbO to metallic lead.

$$PbO + CO = Pb + CO_2.$$

Any unchanged lead sulphide reacts with lead oxide producing metallic lead.

$$PbS + 2PbO = 3Pb + SO_2.$$

The iron ore added reacts with unchanged lead sulphide producing metallic lead and ferrous sulphide.

$$2PbS + Fe_2O_3 + 3C = 2Pb + 2FeS + 3CO.$$

The iron sulphide so formed passes into the slag consisting of calcium silicate and ferrous silicate formed in the following way :—

$$CaCO_3 = CaO + CO_2$$
$$CaO + SiO_2 = CaSiO_3$$
$$Fe_2O_3 + CO = 2FeO + CO_2$$
$$FeO + SiO_2 = FeSiO_3.$$

The molten slag and the molten lead are drawn off through separate tap-holes provided at the bottom of the furnace.

Q. 4. *Describe briefly the manufacture of coal gas. Mention* four *important byproducts and give some account of the uses to which they are put.*

Ans. Coal gas is the gaseous product obtained by subjecting soft coal to destructive distillation. It is a mixture of several

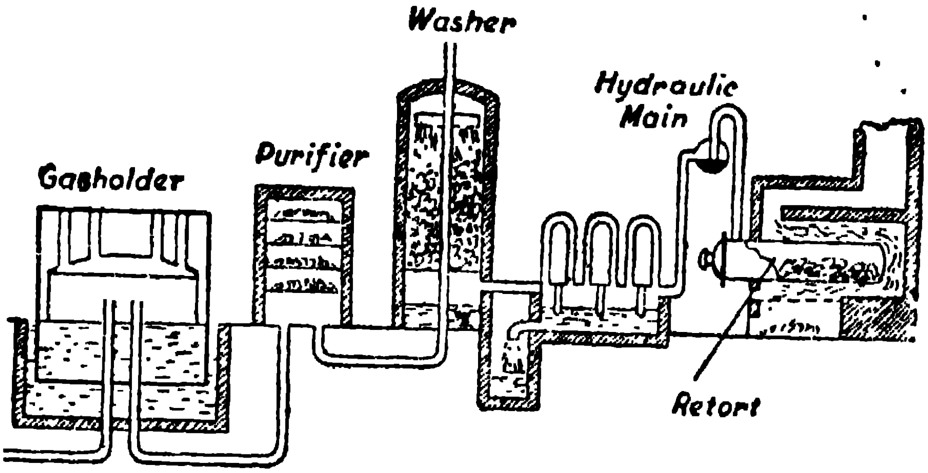


Fig. 115

viz,, Hydrogen, Nitrogen, Marsh gas (CH_4), Ethylene (C_2H_4), Acetylene (C_2H_2), Benzene vapour (C_6H_6), carbon monoxide (CO), Carbon dioxide (CO_2), etc.

Bituminous or soft coal is heated in D-shaped fire-clay retorts, which are fired by the furnace below. The volatile products given off pass up the exit pipes called *ascension pipes* over the retorts. These pipes at the other end are in comunication with the *hydraulic main* where the gas is partially cooled and some tar and water condense. From the hydraulic main the hot gases pass into a series of iron pipes, called *condensers.* Here the gases are further cooled, and more tar is condensed and run into *tar-well.* The liquid in the tar-well separates into two layers—the upper layer is mainly a solution of Ammonia and Ammonium salts in water and is called *gas-liquor* or *Ammoniacal liquor*; the lower layer is called *gas-tar* or *coal-tar.* Next the gases are drawn out of the condensers by means of *pumps* and are forced up a tower filled with coke—called *scrubber*—down which cold water trickles. All traces of ammonia are removed in this way. The gases are next passed through a *purifier* which is an iron tank containing slaked lime, $Ca(OH)_2$, in which CO_2, H_2S and other sulphur compounds are absorbed.

$$Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

A further purification is effected by passing the gases through another purifier containing hydrated oxide of iron which takes up the last traces of H_2S and cyanogen :

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

Thus purified coal gas is stored over water in big gas-holders.

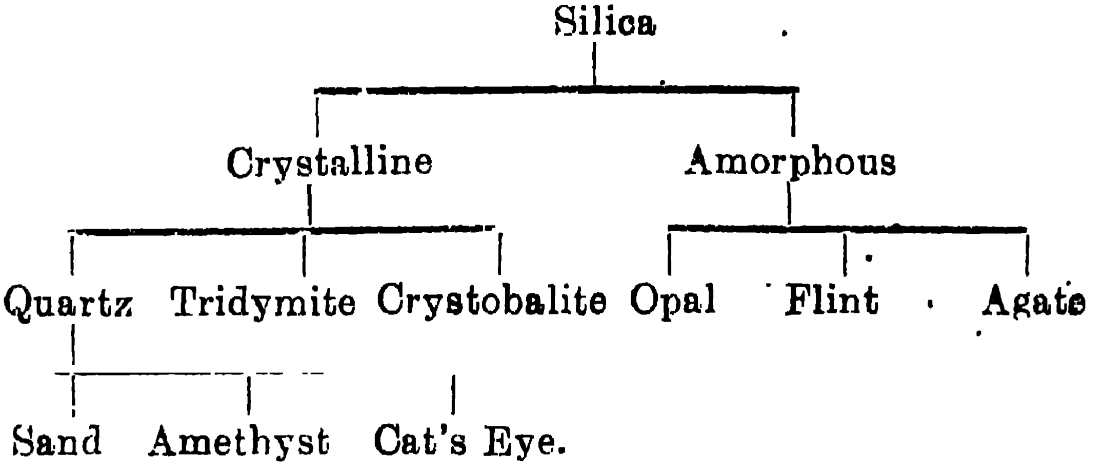
The most important bye-products of coal-gas manufacture are (1) **Gas carbon,** (2) **Ammoniacal liquor,** (3) **Gas lime,** (4) **Coke** (5) **Coal-tar,** (6) **Spent iron oxide.**

Coal-tar is used for preserving timber, and making tarred paper. *Ammoniacal liquor* is used as a source of ammonia and for the preparation of ammonium sulphate which is used as a fertiliser. *Gas lime* is used as a manure. *Coke* is used as a fuel and in metallurgy as a reducing agent. *Gas carbon* is used in electric cells, and in Arc lamps, *Spent iron oxide* is sometimes used for the manufacture of ferro-cyanides, and for generating SO_2 used in the manufacture of H_2SO_4.

Q. 4. Alternative.

How does silica occur in nature ? What are its uses ? How would you prepare silicon from silica ? Write what you know about the allotropic modifications of silicon.

Ans. *Occurrence of silica*—Silica or sand is widely distributed in nature both in the crystalline and amorphous forms. It is present in the crystalline condition as quartz or rock-crystal and also as tridymite and as crystobalite. Many specimens of quartz show beautiful colours and are prized as gems. For example, amethyst is quartz coloured purple by manganese oxide. Silica also occurs in the amorphous state as opal, flint and agate.



Uses of silica :--(1) *Quartz* is used in galvanometers and other electrical instruments ; in the manufacture of chemical apparatus ; and as gems.

(2) *Sand* is used as a building material, in the manufacture of glass, porcelain, etc.

(3) *Agate* is used for making "agate mortars" and for making agate knife-edges for chemical balances. It is also used in making of watches.

(4) *Amethyst* is used as a gem.

Extraction of silicon from silica :—In the laboratory, silicon is most conveniently obtained from silica by heating it with magnesium powder.

$$SiO_2 + 2Mg = 2MgO + Si.$$

After cooling, the magnesia is dissolved out by HCl and the silicon washed in a Pt-dish with HF and H_2SO_4 to remove any unchanged silica.

In industrial practice silicon is produced from silica at Niagra by heating a mixture of Sand and crushed coke in an electric furance, when silicon carbide first formed, according to the reaction $SiO_2 + 3C = SiC + 2CO$, decomposes at about 2400°C., leaving carbon in the form of graphite and silicon liberated is volatilised and condensed.

$$SiC = C + Si.$$

Silicon exists in two different allotropic forms :—

(1) amorphous and (2) crystalline.

Amorphous silicon :—It is prepared by heating strongly an intimate mixture of sand and magnesium powder,

$$2Mg + SiO_2 = 2MgO + Si.$$

It is a brown powder of sp. gr. 2·35. It is a non-conductor of electricity and fuses at 1550°C. When heated in air, it catches fire and burns to SiO_2. It slowly decomposes steam at a red heat. $Si + 2H_2O = SiO_2 + 2H_2$. It is insoluble in all acids except HF in which it dissolves giving hydro-fluosilicic acid. $Si + 6\ HF = 2H_2 + H_2SiF_6$. Silicon combines directly with fluorine and chlorine, with incandescence and burning, with the production of SiF_4 and $SiCl_4$ respectively.

Crystalline silicon :—It is prepared by passing a slow stream of silicon tetra-chloride vapour over metallic aluminium melted down in an atmosphere of hydrogen. Silicon is set free and dissolves in excess of melted aluminium. The mass is cooled when crystalline silicon separates out. The mass is next treated with HCl to dissolve out the excess of Al.

$$3SiCl_4 + 4Al = 3Si + 4AlCl_3.$$

It is a dark-grey crystalline solid of sp. gr. 2·94. It fuses like the amorphous variety at 1550°C. It conducts electricity to a slight degree. It is chemically less active than the amorphous variety. Even on strong heating it does not burn in oxygen. It is insoluble in all acids except HF. It catches fire and burns when heated in chlorine gas and spontaneously burns in fluorine, the products being $SiCl_4$ and SiF_4 respectively.

Q. 5. *Write a short essay on Mendeleeff's periodic classification.*

Ans. When the methods of determining atomic weights came to be established on firm grounds, there arose the possibility of comparing the atomic weights of elements and their properties, in order to find out some definite relationship between these two. As early as 1817, Dobereiner noticed that in some allied elements, the atomic weights were approximately in arithmetical progression. Thus

$$\left\{\begin{array}{l}\text{Ca}\ldots\ldots 40\\ \\ \text{Sr}\ldots\ldots 88\\ \\ \text{Ba}\ldots\ldots 137\end{array}\right\}\begin{array}{l} \\ 48\\ \\ 49\\ \\ \end{array}\quad \left.\begin{array}{l}\text{Li}\ldots\ldots 7\\ \\ \text{Na}\ldots\ldots 23\\ \\ \text{K}\ldots\ldots 39\end{array}\right\}\begin{array}{l} \\ 16\\ \\ 16\\ \\ \end{array}\quad \left.\begin{array}{l}\text{S}\ldots\ldots 32\\ \\ \text{Se}\ldots\ldots 78\\ \\ \text{Te}\ldots\ldots 127\end{array}\right\}\begin{array}{l} \\ 47\\ \\ 48\\ \\ \end{array}$$

These were called *Dobereiner's Triads.*

Almost half a century later, in 1864, the English Chemist Newlands made a remarkable observation that if elements were arranged in the ascending order of their atomic weights, counting from any one of them, the eighth member would be analogous in properties. This was called by Newlands the "**Law of Octaves**" from the analogy with the musical scale.

In 1869 Lothar Meyer, a German Chemist, and simultaneously, but quite independently, the Russian Chemist, Mendeleeff discovered that when the elements are arranged in the order of increasing atomic weights, their properties vary from member to member in a definite way, but return more or less to the same value at fixed points in the series.

If the sixteen elements with lowest atomic wts., after hydrogen, be arranged in order of increasing atomic wts. in two horizontal rows of eight, some of these relations will be recognised—

He = 4, Li = 7, Be = 9, B = 11. C = 12, N = 14, O = 16, F = 19.
Ne = 20, Na = 23, Mg = 24, Al = 27, Si = 28, P = 31, S = 32, Cl = 35·5.

In traversing from He to F in the upper row, we meet with certain characteristic properties belonging to each member, and also a certain gradation in those properties that are common. Coming to the second row, many of the characteristic properties of the members of the first row again appear, and the same regular modulation is met with in passing along the series: thus helium exhibits a likeness to neon, lithium resembles sodium, carbon corresponds to silicon, fluorine to chlorine. These resemblances are seen both in the physical as well as in the chemical properties of the elements, thus lithium and sodium are both soft white metals, and are strongly electropositive. Fluorine and chlorine are both pungent corrosive gases, and are intensely electro-negative, while helium and neon are neither electro-positive nor electro-negative, have no chemical properties whatever, and therefore no valency.

Regarding, then, the eight elements of the first row as a period, we find that the various properties exhibited by the several members are met with again in those of the second period.

Not only do the properties of the elements themselves reappear but also those possessed by the various compounds they form : thus lithium chloride (LiCl) and sodium chloride (NaCl) strongly resemble one another. The oxides of beryllium and magnesium (BeO and MgO) have similar properties. The compounds of fluorine and chlorine with hydrogen (HF and HCl) resemble each other, and so on.

This periodic reappearance of similar properties, exhibited by the elements and their compounds as the atomic weights of the former gradually increase, is thus stated by Mendeleeff in his **Periodic Law** :—"*The properties of the elements, as well as the properties of their compounds, form a periodic function of their atomic weights.*"

When the tabulation of the elements on this basis is continued after the completion of the second period with chlorine, it will be seen that, beginning with argon, eighteen elements have to be arranged before we meet with the reappearance of those properties that belong to the first :—

A	K	Ca	Sc	Ti	V	Cr	Mn	(Fe	Co	Ni)
40	39	40	45	48	51	52	55	56	59	59
Cu	Zn	Ga	Ge	As	Se	Br				
63·5	65	70	72	75	79	80				

This constitutes what is known as a *long period*, in contradistinction to the two first, which are distinguished as *short periods*. In certain respects, however, the last seven elements in this long period exhibit certain amount of resemblances to the seven in the first portion (counting after Argon) ; that is to say, the properties displayed by the members of the first short period, which is known as the *typical period*, reappear twice over in the long period. The three elements within the brackets were termed by Mendeleeff *transitional elements*.

Continuing the arrangement from bromine, another long period occurs, again containing the transitional elements :—

Kr	Rb	Sr	Y	Zr	Cb	Mo	Ma	(Ru	Rh	Pd)
83	85	87·6	89	90·7	93·5	96	—	101	103	106

Ag	Cd	In	Sn	Sb	Te	I
108	112	115	119	121·7	127·5	126·9

After Iodine comes Xenon and then beginning with Xenon, thirty-two elements have to be traversed before we can meet with the same sequence of properties. This period, containing 32 elements with another set of three transitional elements and 15 rare-earth elements, is called a *very long period or a monster period.* The rare-earth elements are all placed in one group.

Then comes a fragmentary period containing only 6 elements all of which are *radio-active.* It ends with Uranium, the element with the highest atomic weight known.

Those elements that fall in the first eight places of the long periods are stated to form the *even series*, while the last seven are distinguished as forming *odd series.*

In this manner the elements are arranged in nine vertical *groups*. The first of these groups contains the so-called "inert gases". And as the system of numbering the groups of elements in their periodic arrangement has become familiarised by long use, this group containing the "inert gases" has been numbered Group O, and the systematic numbering of the other groups begins as usual. The last group, viz., the Group VIII, contains the transitional elements that come between the even and odd series of the long periods.

In each of the remaining seven groups, the elements belonging to the even series of their respective long periods, are placed to the left, while those belonging to the odd series are arranged on the right-hand side of each vertical column. In this way the groups are divided into the sub-divisions A and B, in which the resemblance between the members is most pronounced. Thus, in Group II, although there are certain properties common to all the members there is a much closer similarity existing between the elements calcium, strontium and barium than between zinc and calcium, cadmium and barium. The elements in the two short periods have been placed in the sub-division with the members of which they exhibit the closest resemblance. Thus, in Group I, lithium and sodium are more allied to potassium, rubidium, and caesium, than to copper, silver and gold ; while in Group VII fluorine and chlorine are placed in the same family with bromine and iodine, with which they exhibit a close similarity.

Periodicity in the properties of the elements, when arranged in the Periodic Table is shown by the physical properties like melting point, boiling point, specific gravity, conductivity for heat and electricity etc., and is best illustrated by the atomic volume curve. Atomic volume of an element is $\frac{\text{At. wt.}}{\text{Sp. gr.}}$ of the element. When the values for atomic volumes are plotted against at. wts. of elements, with at. wts. as abscissæ and at. volumes as ordinate, a curve is obtained, which is distinctly periodic.

The periodicity in the chemical properties of the elements when arranged in the Periodic Table is seen by taking into consideration *Valency* and *electro-chemical character* of the elements.

(*a*) *Valency*—The elements of group O have zero valency. The valencies of the elements towards hydrogen increases regularly from 1 to 4 while passing from Group I to Group IV and then diminishes from 3 upto 1 from Group V to Group VII, as is evidenced from the formation of compounds like

$$LiH, CaH_2, (BH_3)_2, CH_4, NH_3, SH_2, FH.$$

The valencies towards oxygen, on the other hand, increase regularly from 1 to 8 as we pass on from Group I to Group VIII, as illustrated by formation of compounds like

$$Li_2O\ BeO\ B_2O_3\ CO_2\ N_2O_5\ SO_3\ Cl_2O_7\ OsO_4.$$

(*b*) Electro-chemical character—In Group I we find the elements which are highly *electro-positive.* Then gradually the electro-positive character diminishes until in Group IV we find elements like C, Si, etc., which are *electrically indifferent.* Then from Group V upto Group VII the *electro-negative* character makes its appearance and the elements of Group VII are highly electro-negative. Then from highly electro-negative elements like F or Cl, the transition to the highly electro-positive elements like Na or K takes place through element like Ne or A which have no valency and therefore of electrical character infinity. Hence a regular periodicity is exhibited in electro-chemical character when we consider the elements as arranged in the periodic table.

Usefulness of the Periodic Table :—

The uses of the Periodic system is found :

1. *In the classification of the elements.*—It is the best of all the modes of classifying the elements. It. has rendered the study of about 90 elements into that of nine vertical groups.

2. *In correcting doubtful Atomic weights.*—One example will make this clear. The equivalent weight of Indium was found to be 38. Its. at. wt. was taken as $2 \times 38 = 76$. In that case Indium is to be placed between Arsenic and Selenium. But there was no room for such an element there. Mendeleeff, judging from its properties, suggested that Indium should have an atomic weight $3 \times 38 = 114$ which would place it between Cadmium and Tin, where it fits very well. The subsequent determination of the atomic heat of Indium and thence its at. wt. corroborated this change and the correct at. wt. of Indium is taken as 114 and not 76.

3. *In the prediction of new elements.*—At the time when the Periodic law was first formulated, there were three gaps in the system in the first long period, viz., No. 4 in the even series (now occupied by Scandium), and Nos. 3 and 4 in the odd series (now filled by Gallium and Germanium). To the unknown elements which were destined to occupy those positions, Mendeleeff gave the names *eka-boron*, *eka-aluminium*, and *eka-silicon* and from the known properties of the neighbouring elements of the series and also of those situated nearest in the same family, he predicted some of the prominent properties that would probably be possessed by these elements. These predictions came out to be true when in 1875 Lecoq de Boisbaudran discovered Gallium tallying in properties with eka-aluminium. Discovery of Scandium (Nilson, 1879) and Germanium (Winkler, 1886) whose properties were found to closely accord with those of eka-boron and eka-silicon respec-

tively, formed an additional demonstration of the truth of the Periodic law.

Defects of the Periodic classification :—

1. The position of Hydrogen is yet open to discussion. It is monovalent and so can be placed either in Group I with the alkali metals or in Group VII with the halogens. The only argument for placing Hydrogen with the alkali metals is that it is an electro-positive element like the alkali metals. Arguments in favour of placing Hydrogen in Group VII with the halogens are :—

(1) Like the first two members of halogen family, viz., F and Cl, it is a gas. (2) Like the halogens, its molecules are diatomic. (3) It may be replaced, atom for atom, from organic compounds, by the halogens. (4) Just as the metals form halides with the halogens, similarly alkali metals and the alkaline earths form definite hydrides as an electro-negative element. (5) If hydrogen be placed in group VII, the difference between the at. wts. of hydrogen and its next congener fluorine is 18 which is the usual difference between the atomic wts. of two successive elements in the same group in the first two short periods ; but this sequence is broken, if it be placed in Group I.

2. In the case of some elements, the atomic weight sequence is broken : thus in three sets

(*a*) Argon (38·9) and Potassium (39·0)
(*b*) Cobalt (58·9) and Nickel (58·6)
(*c*) Tellurium (127·5) and Iodine (126·9)

3. There are fifteen rare-earth elements for which appropriate place have not been found.

4. The periodic classification according to atomic weights overlooks certain chemical analogies. For example,

(*a*) Copper, silver and gold have very little analogies with sodium, potassium, etc. and yet they have been placed in the same group with the alkali metals. Similarly, manganese has been placed in the same group with the halogens.

(*b*) Copper and Mercury, Silver and Thallium, Barium and Lead, which appear to be chemically similar, are placed in separate groups.

FIRST PAPER—1956

Q. 1. *Giving neat sketches of the apparatus used describe* **any two** *of the following processes :—*

(*a*) *Distillation of water,*

(*b*) *Laboratory preparation of* H_2S*,*

(*c*) *Accurate weighing of a substance.*

Ans. (*a*) Distillation of water is carried out with the help of a distilling flask, fitted to a Liebig's condenser and a receiver.

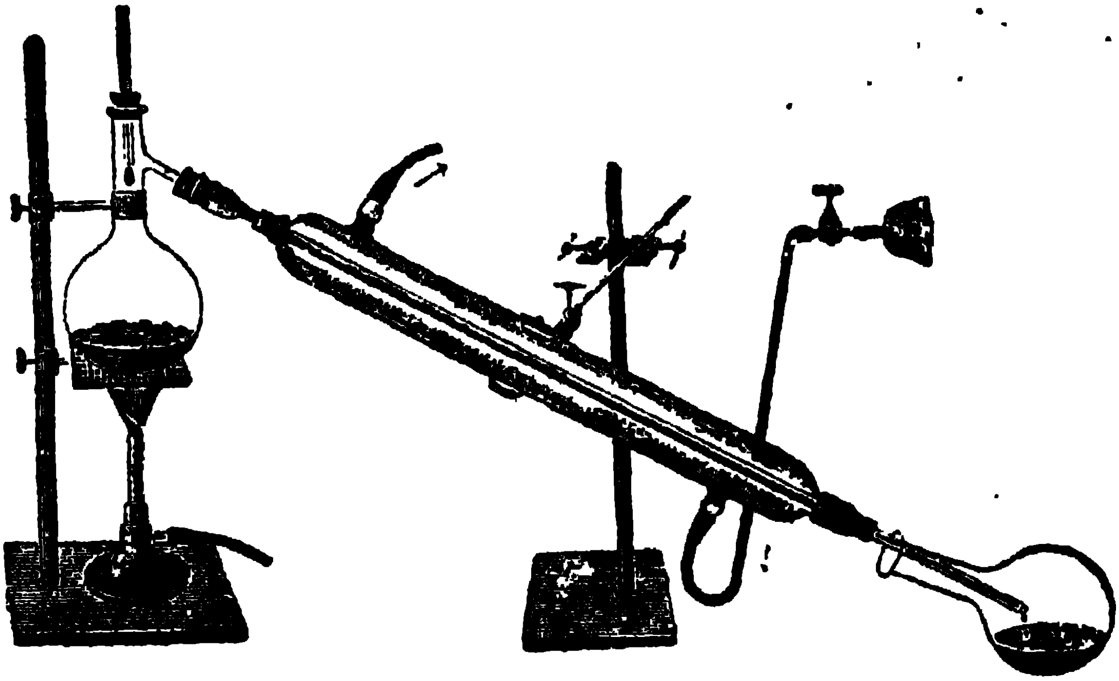


Fig. 116

The appartus is arranged as shown in the adjoining figure. Water is taken in the distilling flask. The side tube of the distilling flask is introduced through a cork, fitting tightly to the condenser tube, into the condenser tube of a Liebig's condenser as shown in the figure. Cold water enters the jacket of the condenser tube by the lower side-tube and after circulating round the narrow inner condenser tube, and getting heated by coming in contact with steam passing through the inner condenser tube, leaves by the upper side tube. The arrangement for this cold water circulation through the jacket tube is shown in the figure. A clean flask (called receiver) is placed at the other end of the condenser tube in such a way that the open end of the condenser tube is well inside the flask. The condensed water collects inside the receiver. A thermometer is introduced into the distilling flask through a cork fitted air-tight to its neck. The bulb of the thermometer is placed slightly below and nearly opposite to the side tube of the distilling flask as shown in the figure. After completing the above arrangement of the different parts of the apparatus for distillation, the distilling flask containing water to be distilled is placed on a wire gauze fitted on the top of a tripod stand and heated by means of a Bunsen flame, till the water in the flask boils. The vapour of water, given off during boiling, passes through the inner tube of the Liebig's condenser and condenses back into liquid water there due to the cooling action of cold water circulating through the jacket-tube and collects inside the receiver after trickling down the inner tube. The water collecting in the receiver is called the *distillate*. The thermometer is used to note the temperature.

(*b*) In the laboratory H_2S is prepared by the action of dilute sulphuric acid on chips of ferrous sulphide, placed in a Woulfe's bottle, or, for continuous supply as required in qualitative analysis, in Kipp's apparatus.

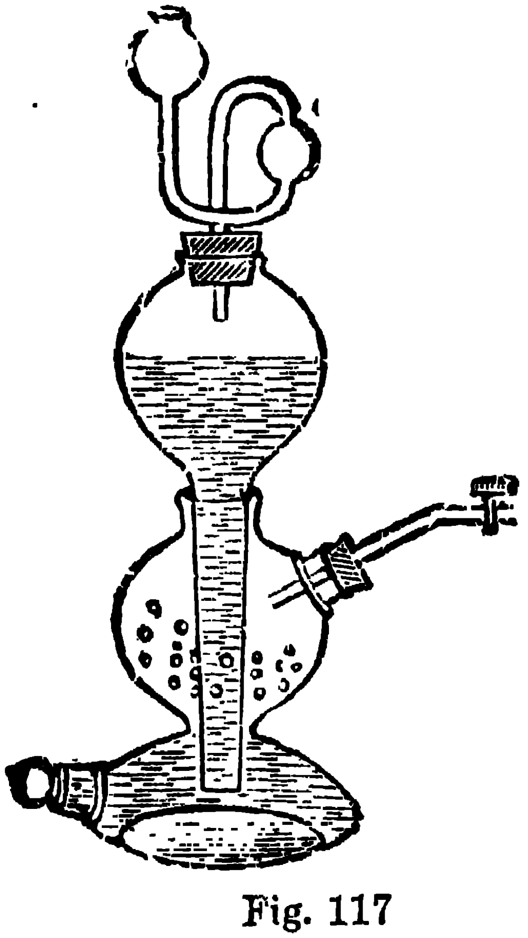


Fig. 117

Ferrous sulphide, FeS, in broken fragments, is introduced into the central globe of a Kipp's apparatus. The stop-cock fitted to the tube attached to the middle globe is opened and dilute H_2SO_4 is poured down the safety funnel at the top of the upper globe, which is fitted to the mouth of the middle globe, after putting in the fragments of ferrous sulphide. The acid runs down to the lowest globe, fills that lowest globe, and then rises into the central globe where it comes in contact with ferrous sulphide. Sulphuretted hydrogen is produced and escapes through the stop-cock.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

When the gas is not required, the stop-cock is closed ; the gas collects in the central globe, and the pressure of the gas forces the acid out of the central globe. The acid rises up the stem and goes to the top-most globe. Thus further reaction stops. When the gas is required, the stop-cock is opened, H_2S escapes, the acid comes down from the top-most globe and so the contact between FeS and H_2SO_4 is brought about. Then fresh quantities of H_2S are evolved.

(*c*) For very accurate weighing, especially in Chemical Analysis, a sensitive chemical balance is always used. It is a very delicate apparatus. So it should be handled very carefully. It is specially constructed to produce extreme sensitiveness and

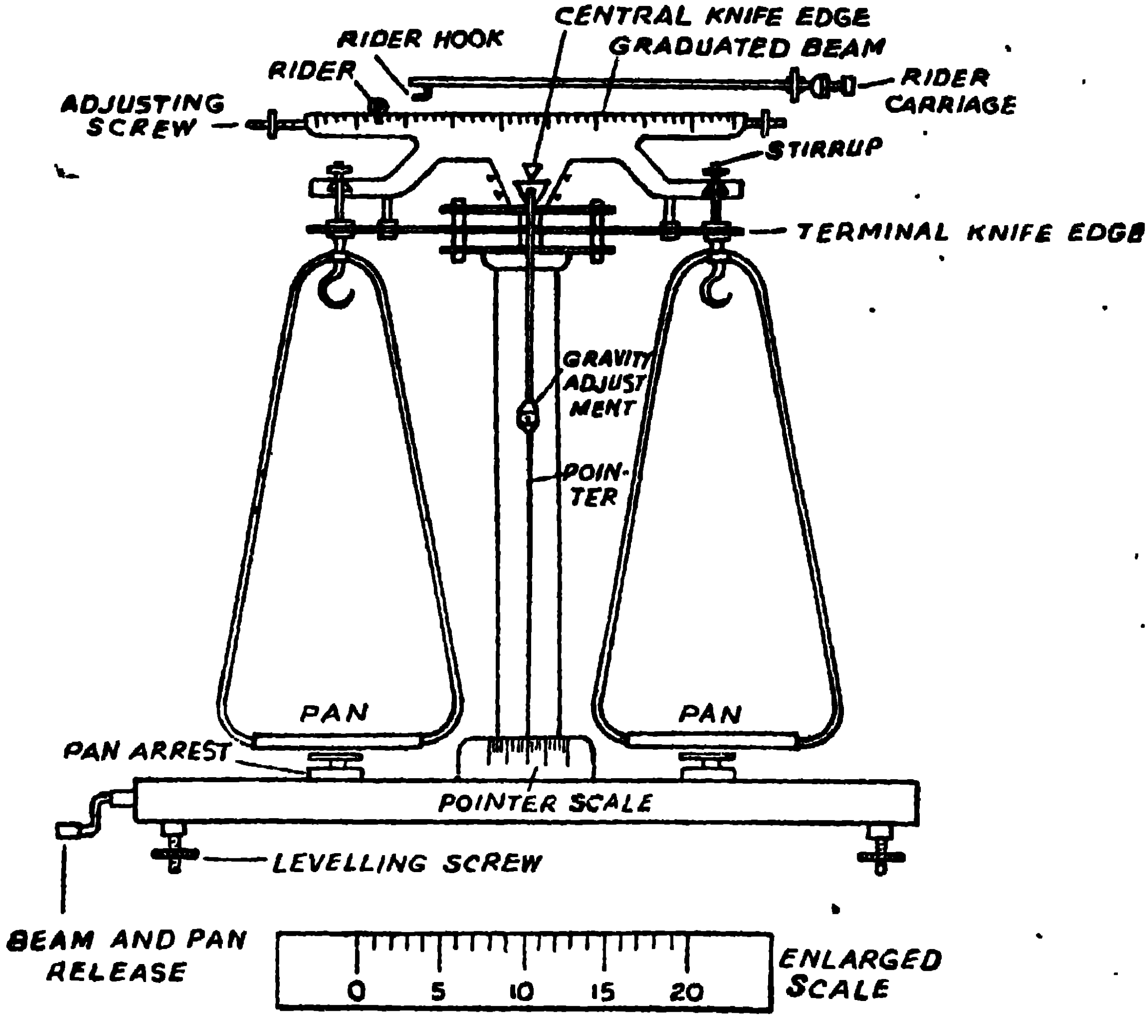


Fig. 118

hence it is kept in glass cases the interior of which is kept dry by placing a beaker containing fused Calcium chloride in one corner. By this arrangement the balance is protected from dust and draught.

The essential features of a typical chemical balance are shown diagrammatically in the adjoining figure. The beam of the balance is so constructed that it is as rigid and light in weight as possible and it is mounted at its centre upon a prism-form agate knife-edge which rests upon an agate plate attached to the central beam support. There are two agate knife-edges at the two ends, fixed at equal distances from the central knife-edge and a stirrup is suspended from each of them. The pans are hung from these stirrups, contact being made upon agate planes fixed to the stirrups. A long pointer is attached to the centre of the beam and this moves over a scale at the foot of the pillar. The movement of this pointer on the scale indicates the deflection of the beam from the horizontal position when the balance is in operation. The balance, before being operated, is to be levelled with the aid of levelling screws and a plumb line suspended from the column (or with spirit level fixed to the base of the balance). The whole of the beam is divided into 100 equal parts (in Bunge type) with O of the scale on the left-hand side of the user and into 50 equal parts on either side (in Sartorius type) with O of the scale in the middle, so that weight adjustments smaller than 10mg. can be made readily with the help of a small piece of platinum or gilded aluminium wire (called the *rider*) placed on the beam and moved along the beam by means of a *rider carrier* (a sliding metal rod which is worked from outside the balance case). For the Bunge type of balance a 5 mg. rider is employed ; in the Sartorius type a 10 mg. rider is necessary. A small weight is attached to the pointer for altering the sensitivity of the balance. There are adjusting screws at the ends of the beam for the purpose of adjusting the equilibrium position of the pointer so that it rests at the centre of the scale ; this ensures that the beam is horizontal when unloaded. In order to protect the knife edges from undue wear and tear during the transfer of weights and objects, the balance is provided with a device by means of which the moving parts can be raised, thus slightly separating the knife edges and planes. The device is operated by means of a large screw attached to the base of the balance, placed either centrally in the front of the base, or in the centre of the left-hand side of the base. In many balances there are separate *beam arrest* and *pan arrest*; but these two are generally combined in a single device.

For accurately weighing a substance an analytical weight-box, containing calibrated weights, is required. The weights range from 50 grams upto ·01 gram, the arrangement being 50, 20, 20, 10, 5, 2, 2, 1 grams, 0·5, 0·2, 0·2, 0·1, ·05, ·02, ·02, ·01 grams (fractional weights). With the help of the rider the weight of the substance is determined upto the fourth place of decimal in grams.

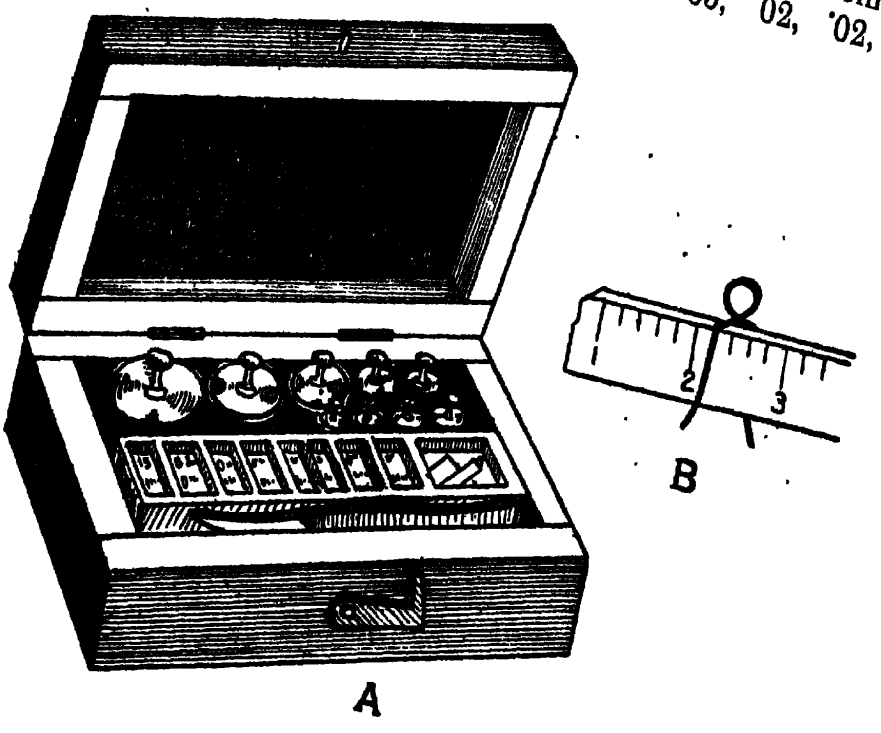


Fig. 119

Before use, the balance is first of all tested for correctness. This is done in the Bunge type by placing the rider at O mark of the scale on the beam and the pans are set in motion by lowering the screw head. The same operation is carried out in the Sartorius type with or without the rider on the O mark.

The pointer oscillates equally on both sides of the O mark of the scale and thereby indicates the correctness of the balance. The substance to be weighed is then placed on the left-hand pan of the balance and weights are added to the other pan until the smallest weight added on the pan is within ·01 gram. The final adjustment is made with the rider, so that the beam returns to its original equilibrium position. The weights required are then noted down. The sum-total of these weights is the weight of the body.

Q. 2. *Write what you know about* **any two** *of the following :—*

(*a*) *Crystals—How are they obtained ? What is water of crystallisation ?*

(*b*) *Kinds of matter and energy—their indestructibility.*

(*c*) *Solubility—unsaturated, saturated and supersaturated solutions.*

Give examples wherever necessary.

Ans. (*a*) Crystals are defined as homogeneous solids usually having definite geometrical forms ; these break into pieces with plane faces meeting in sharp edges.

Crystals are usually obtained (*i*) by cooling or evaporating a saturated solution of a solid. Thus crystals of copper sulphate, $CuSO_4, 5H_2O$ (blue virtriol) can be obtained by preparing a clear saturated solution of the material in a basin, evaporating the solution until solid crystals begin to appear at the edges, and then cooling the solution to room temperature.

(*ii*) By fusing a solid and then allowing it to cool and solidify, e.g., when ordinary roll sulphur is fused in a crucible and the crucible cooled, a solid crust appears on the surface. On piercing holes into the crust and pouring out the still liquid portion, prismatic crystals of sulphur are obtained.

(*iii*) By condensing the vapour of a volatile solid. Thus, iodine crystals can be obtained by heating iodine in a basin, kept covered with a funnel when iodine sublimes and is deposited in shining crystals in the funnel.

Many solids, when crystallising out from their aqueous solutions, combine chemically with a definite number of molecules of water. This chemically-combined water can be driven off more or less easily by heating and when this is driven off the particular crystalline shape is lost and the solids fall to powder. Sometimes colour of the crystalline solid is removed. Water thus associated with crystals as an essential part of their constitution, is called *water of crystallisation.*

Thus, in crystals of copper sulphate, $CuSO_4, 5H_2O$, 5 molecules of water are present as water of crystallisation. On heating, these water molecules are removed and blue crystals are transformed into white powder.

(*b*) Matter can be of three kinds, solid, liquid and gaseous. A solid has a definite mass, volume and shape. A liquid has a definite mass and volume, but no shape ; when at rest it takes the shape of that part of the vessel in which it is contained. A gas has a definite mass, but no definite volume or shape ; it completely fills and takes the shape of the containing vessel.

Water is the most familiar example of matter existing in nature in the three states, ice (solid), water (liquid) and vapour (gas). Matter may pass from one kind to another by heat or cold. Thus ice when heated becomes water which when further heated becomes steam.

Different kinds of energy met with in nature are :—

(*i*) Mechanical energy ; (*ii*) Heat ; (*iii*) Sound ; (*iv*) Light ; (*v*) Electrical ; (*vi*) Magnetic ; (*vii*) Chemical. It is to be noted that all these forms of energy can be divided into two classes—kinetic and potential, and one form of energy frequently changes into another form.

Matter is indestructible, and so the total quantity of matter in every chemical action is exactly the same after the change as the total quantity of matter taking part in the reaction before the change.

The law of indestructibility of matter is proved by the following experiment :—A round bottomed flask is provided with a tightly fitting rubber cork. Through the cork two thick copper wires carrying a copper spoon at the end are fitted. A little bit of charcoal is placed on the copper spoon. The two thick copper wires near the spoon are wound round with a thin platinum wire so that the two copper wires are in contact through the Pt-wire and the platinum wire is made to touch the piece of charcoal. The rubber cork with the copper wires carrying the spoon is removed, and the air inside the flask is replaced by oxygen. The cork with the wires carrying the spoon in which the piece of charcoal is placed, is then replaced in its original position so that it tightly closes the mouth of the flask. Then the flask with its contents is weighed in a chemical balance. The copper wires projecting outside the cork are then connected to the terminals of a battery, and a current is passed. The Pt-wire becomes red-hot due to resistance offered by this thin wire and this ignites the piece of charcoal in contact with it and it burns readily in the oxygen gas. After the flame is extinguished, the wires connecting the battery are disconnected, the apparatus cooled and weighed in a chemical balance. The weight is found to be the same as before. Thus, although most of the bit of charcoal has disappeared by burning, yet no loss in weight is recorded. Hence nothing is lost by burning away of the piece of charcoal.

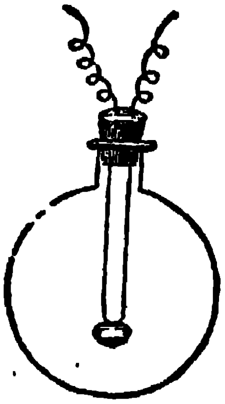


Fig. 120

Energy is also indestructible. It can be transformed from one form into the other, but the sum-total of energy always remains the same ; it can neither be created nor destroyed.

(*c*) Solubility of any substance in a solvent at any particular temperature is the weight in grams of the substance which when dissolved in 100 grams of the solvent forms a saturated solution at that particular temperature.

A solution which retains its concentration unchanged when it is in contact with excess of solute at a fixed temperature is called a *saturated* solution. When the concentration of the solution increases by placing it in contact with the solute, it is said to be *unsaturated* and when the concentration of the solution decreases by being placed in contact with the solid solute, it is said to be *supersaturated*.

Thus, when potassium nitrate in small amount is added to a quantity of water taken in a beaker, it dissolves. We get an unsaturated solution of nitre now. The addition of potassium nitrate is continued till an appreciable quantity remains undissolved. The beaker with its contents is then heated by being placed on a wire-gauze. Further quantity of nitre dissolves. The solution is then cooled to room temperature when certain amount of solid nitre is deposited. The solution so obtained is a saturated one at room temperature. Crystals of sodium thiosulphate are taken in a flask and the flask is gently heated. The crystals melt in their own water of crystallisation and a very concentrated solution of sodium thiosulphate is obtained. On cooling to room temperature, after plugging the mouth of the flask with a tight cork, no separation of crystals takes place. The solution so obtained is a supersaturated solution of sodium thiosulphate, because on adding a tiny crystal of sodium thiosulphate to the solution and shaking, the whole liquid solidifies with evolution of heat.

Q. 3. *Describe, with a neat sketch of the apparatus used, the laboratory preparation of Ammonia. Give tests to demonstrate its principal properties. How would you prove that Ammonia is composed of three volumes of Hydrogen and one volume of Nitrogen ?*

Ans. Preparation of *dry* ammonia in the *laboratory* is carried out by heating *dry* powdered ammonium chloride with about twice its weight of powdered quicklime in a hard glass test-tube closed by a cork through which a delivery tube is fitted. The hard glass test-tube is clamped in a slightly inclined position to a retort-stand and the delivery tube is joined to the bottom of a lime-tower, filled with quicklime, as shown in the figure. An upright delivery tube is next fitted to the top of the lime-tower as shown in the figure. Ammonia, evolved and dried in lime-tower, is collected by downward displacement of air.

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

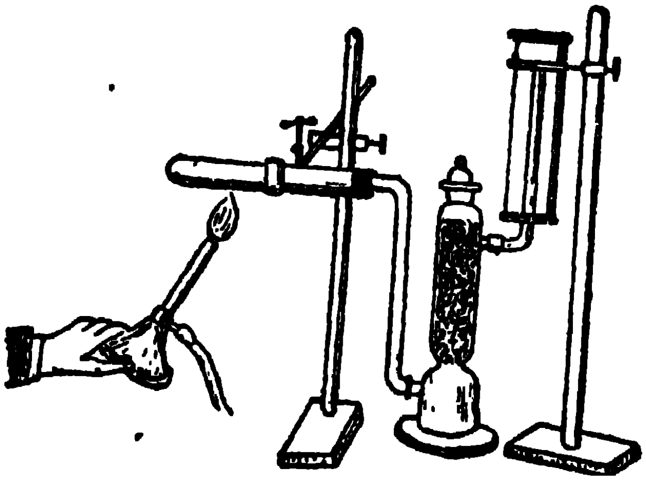


Fig. 121

Tests demonstrating the principal properties of ammonia :—

(*i*) The gas is smelt. It is found to possess a peculiar pungent odour.

(*ii*) The gas is collected by downward displacement of air. This shows that the gas is lighter than air.

(*iii*) A test-tube is filled with the gas by downward displacement of air. The ammonia-filled test-tube is then inverted over a trough of water. It is found that water rises and fills the tube very rapidly. This proves that the gas is extremely soluble in water.

(*iv*) To the aqueous solution of ammonia, a drop of a solution of litmus rendered red with acid is added. The colour of the solution becomes blue. This proves the alkaline character of ammonia. Perhaps ammonium hydroxide is formed by combination of ammonia with water :

$$NH_3 + H_2O = NH_4OH.$$

(*v*) The gas is collected in a gas-jar by downward displacement of air. A lighted taper is introduced in the gas by holding the jar with mouth downwards. The taper is extinguished and the gas does not burn. This shows that ammonia is neither a supporter of combustion nor combustible in air.

(*vi*) A glass chimney is fitted at its bottom with a cork and two glass tubes, one long and another short, are fitted into the chimney through the cork in such a way that the longer one reaches the top of the chimney and the shorter.one just projects beyond the cork. A small quantity of cotton wool is placed on the cork in the form of a pad. At first oxygen is passed through the short tube and then dry ammonia through the long tube and the mouth of the chimney closed for few seconds with the palm of the hand. The palm is next removed and a lighted taper is applied to the mouth of the long tube. Ammonia catches fire and burns with a yellowish flame.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

(*vii*) A few drops of concentrated HCl is poured into a gas-jar which is then closed with a cover glass. The gas-jar is shaken well and the excess of conc. HCl is poured out. It is then placed mouth to mouth with another gas-jar containing ammonia and the cover-plates of the two gas-jars removed. Dense white fumes at once appear in both the jars and these settle down ultimately to solid ammonium chloride.

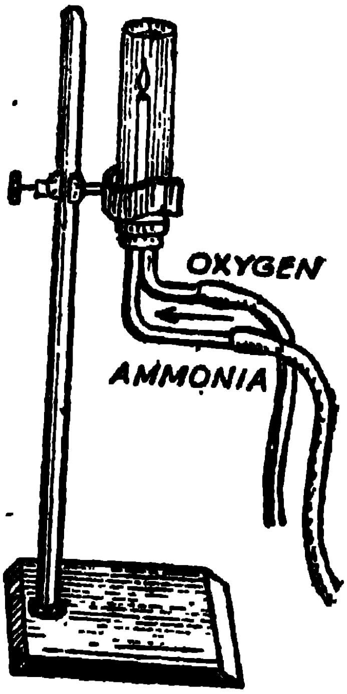


Fig. 122

$$NH_3 + HCl = NH_4Cl.$$

(*viii*) A hard-glass tube is packed with black copper oxide and it is heated in a furnace. When CuO becomes red-hot, ammonia gas is passed over it. Red metallic copper appears in the hard-glass tube. This proves that ammonia acts as a reducing agent.

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2.$$

The composition of ammonia is determined by Hoffmann's method.

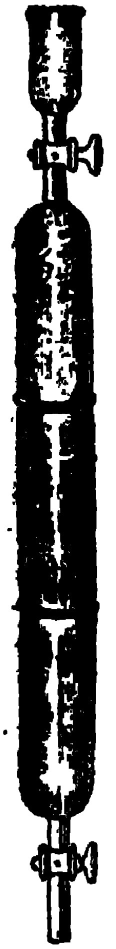


Fig. 123

The fact that ammonia is decomposed by chlorine producing N_2 and forming NH_4Cl is taken advantage of in this method to show the volumetric composition of ammonia.

A long glass tube fitted with a stop-cock at one end and a small dropping funnel at the other, is marked off into three equal divisions by India-rubber rings (Fig. 121). The tube is completely filled up with chlorine gas. A strong solution of ammonia is admitted into the tube drop by drop from the funnel until the reaction between the chlorine and ammonia, ceases. Chlorine combines with the hydrogen of ammonia giving HCl and nitrogen is set free. HCl now reacts with excess of ammonia producing white fumes of NH_4Cl.

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

When an excess of ammonia has been added to ensure its complete conversion into NH_4Cl and N_2, the excess of ammonia is neutralised by adding dilute H_2SO_4 in excess. The stop-cock of the dropping funnel is now turned off, and the tube is placed in a tall jar containing water. The bottom stop-cock is now opened, when water rushes up and fills the tube nearly upto the second mark from the bottom. The level of water inside and outside the tube is now made the same, when the residual gas is found to occupy one-third of the vol. of chlorine taken. That the residual gas is Nitrogen is proved by the facts that it is inert, it does not readily combine with other elements and it is absorbed by strongly heated Magnesium.

We know that Hydrogen and Chlorine combine in equal volumes to form HCl gas. Therefore, 3 vols. of Chlorine taken in the tube, must have combined with 3 vols. of Hydrogen. These 3 vols. of Hydrogen must have come from Ammonia gas, which has simultaneously liberated 1 vol. of Nitrogen. Thus, *ammonia is made up of one volume of nitrogen combined with three volumes of Hydrogen.*

Q. 4. *How would you explain the following :—*

(a) *When a flask (dried outside) containing water is heated by a Bunsen burner moisture always accumulates on the outside surface.*

(*b*) *In the flame test we cannot use copper wire in place of platinum wire or asbestos fibre.*

(*c*) *Hydrofluoric acid cannot be kept in a glass bottle.*

(*d*) *Ammonia bottle should always be kept tightly stoppered, away from a bottle containing strong Hydrochloric acid in the laboratory.*

(*e*) *Effervescence occurs when acids drop on the cement floor.*

Ans. (*a*) In a Bunsen burner, the combustible coal gas or kerosene gas (in mofussil towns) is burnt. Now, coal gas or kerosene gas contains hydrogen and hydrocarbons like CH_4, C_2H_4, C_2H_2, C_6H_6, etc. When they burn in air, steam is formed. This steam, coming in contact with the cold surface of the flask containing cold water, condenses to droplets of water and so moisture accumulates on the outside surface of the flask.

$$2H_2+O_2=2H_2O.$$

$$C_xH_y+\left(x+\frac{y}{4}\right)O_2=xCO_2+\frac{y}{2}H_2O.$$

(*b*) Copper wire cannot be used in performing the flame test for detecting a basic radical in an inorganic sample because when dipped into conc. HCl (for cleansing the wire) and held in the non-luminous Bunsen flame, it imparts greenish blue coloration to the flame. This coloration will mask the coloration produced by most other basic radicals capable of imparting coloration to the flame. Platinum wire or asbestos fibre does not suffer from this disadvantage after cleansing with conc. HCl in the flame.

(*c*) Glass is a mixture of several silicates. Hydro-fluoric acid has the capacity of dissolving silicates. On that account the glass bottle will be eaten away by hydro-fluoric acid and ultimately perforations will take place and the acid will run out.

Soda-lime glass is Na_2O, CaO, $6SiO_2$. The reaction that takes place with HF can be represented as

$$Na_2O, CaO, 6SiO_2+28HF=2NaF+CaF_2+6SiF_4+14H_2O.$$

(*d*) Ammonia bottle contains a concentrated solution of ammonia in water, which smells strongly of ammonia on account of the spontaneous escape of gaseous ammonia from the solution. On this account the bottle should be kept tightly stoppered, otherwise ammonia gas will escape from the bottle by pushing the stopper up, when it is loosely fitted, by the pressure generated inside the bottle due to escape of gaseous ammonia from the solution. The bottle of ammonia for the same reason, is to be kept away from a bottle containing strong Hydrochloric acid in the laboratory, for any ammonia gas escaping from the ammonia bottle will form dense white fumes of ammonium chloride with Hydrochloric acid vapour escaping from bottle containing concentrated Hydrochloric acid which is nothing but a strong solution of Hydrogen chloride in water.

$$NH_3 + HCl = NH_4Cl.$$

(e) Cement is a complex calcium aluminium silicate. During the preparation of the floor, it is used along with water and so, due to hydrolytic decomposition, some lime, $Ca(OH)_2$ is produced from cement. This lime then absorbs atmospheric carbon dioxide and is converted into calcium carbonate. When acids drop on the floor, this calcium carbonate reacts with acids, evolving carbon dioxide with effervescence.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Q. 5. *How would you prepare* **any two** *of the following* :—

(a) *Sulphur trioxide*, (b) *Ozone*, (c) *Hydroiodic acid.*

Give their principal tests with chemical reactions and equations where necessary.

Ans. Sulphur trioxide is prepared on a large scale from sulphur dioxide by passing a mixture of sulphur dioxide and excess of oxygen in the form of air, freed from dust, sulphur particles, arsenious oxide, etc., and dried properly, through a

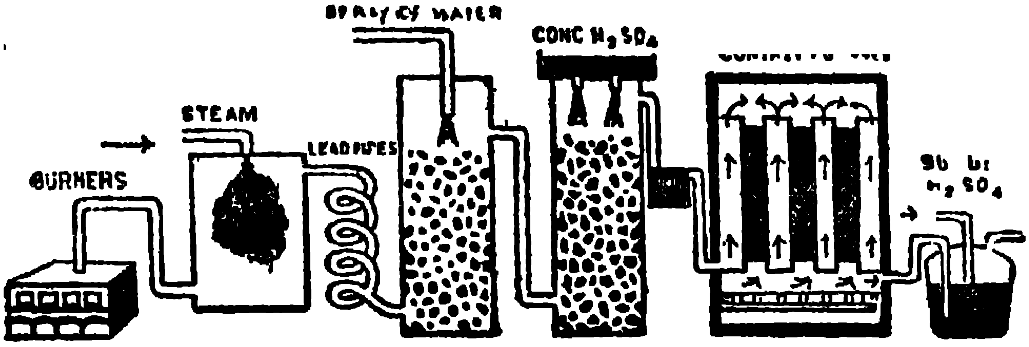


Fig. 124

contact furnace containing platinised asbestos heated by ring burners to a temperature of 450°C at the start. The contact furnace consists of an iron box fitted with vertical iron pipes packed with the platinised asbestos. The heating is discontinued as the reaction proceeds, for the heat of the reaction maintains the temp. necessary for the reaction. Platinised asbestos acts as the catalytic agent and sulphur dioxide is oxidised to sulphur trioxide by atmospheric oxygen. A white cloud of sulphur trioxide escapes through the other side of the furnace. This white cloud is passed through a well-cooled receiver where sulphur trioxide condenses in the form of white silky needles.

$$2SO_2 + O_2 = 2SO_3.$$

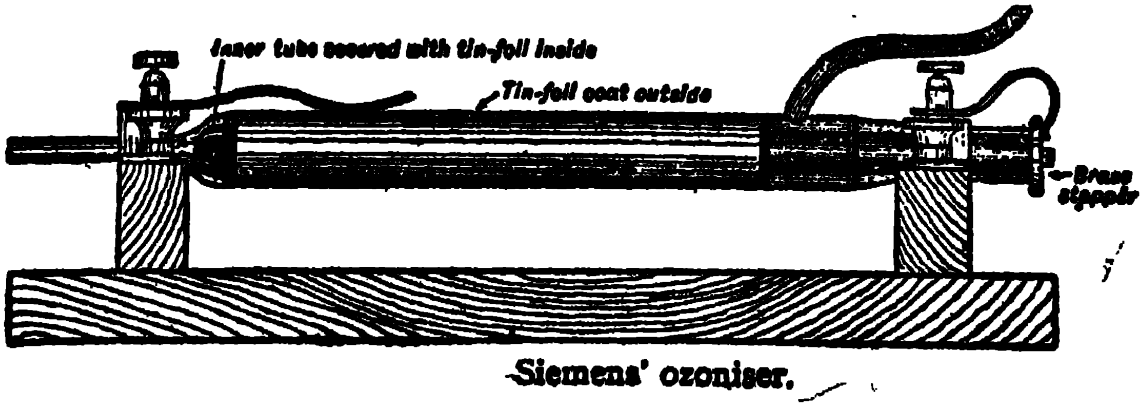
Tests :—(i) When thrown on to water, a sound like the quenching of red-hot iron is produced and much heat is evolved, which converts water into steam.

$$SO_3 + H_2O = H_2SO_4.$$

(ii) The solution so produced, when treated with Barium chloride solution, deposits heavy white precipitate of Barium sulphate insoluble in conc. HCl.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$$

(*b*) Ozone is best obtained by exposing pure dry Oxygen to the action of silent electric discharge in Siemen's Ozoniser which consists of two concentric glass tubes. The outer tube is coated outside and the inner lined inside with tinfoils. These tinfoils are connected with two binding-screws which in their turn are in connection with a Ruhmkorff's coil. Dry oxygen is passed through the annular space in slow stream and a series of silent



Siemens' ozoniser.

Fig. 125

electric discharge is passed. The gas coming out at the exit consists of a mixture of oxygen and ozone.

$$3O_2 = 2O_3$$

Tests :—(i) The fishy odour of the gas helps to identify it.

(ii) Moist starch-iodide paper, when held in the gas, is turned blue due to liberation of iodine by oxidation of KI.

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2$$

(iii) Paper soaked in an alcoholic solution of *tetramethyl base* is turned purple or violet by ozone.

In the laboratory hydriodic acid is prepared by dropping water from a dropping funnel, fitted to a flask containing a mixture of red phosphorus and iodine. The flask is provided with a delivery tube and the delivery tube is connected to U-tube containing glass beads and moist red phosphorus. The flask is cooled by dipping in water. Hydriodic acid gas mixed with iodine vapour is evolved in the flask and in passing through the U-tube containing moist red phosphorus iodine vapour is absorbed. The HI gas is then collected by upward displacement of air.

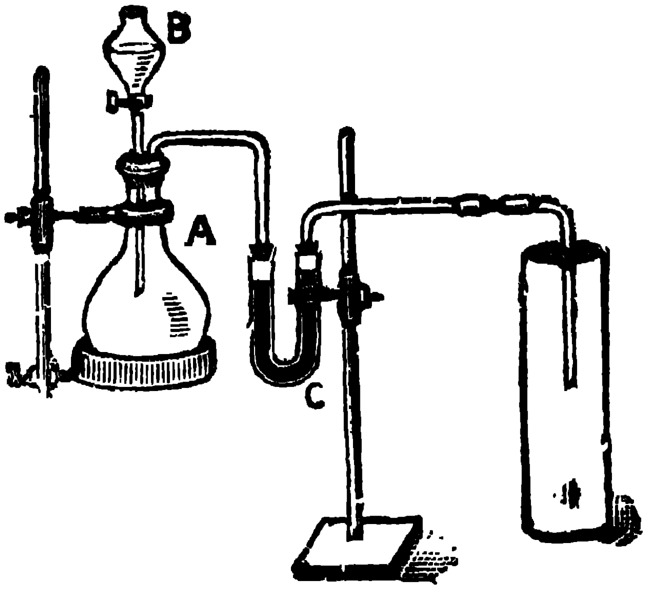


Fig. 126

At first phosphorus tri-iodide is formed, which is then decomposed by water forming phosphorous acid and hydriodic acid.

$$P + 3I = PI_3. \quad PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

When an aqueous solution of the acid is required, the delivery tube from the U-tube is connected to an inverted funnel, which in its turn is dipped into water contained in a beaker.

This arrangement is employed for preventing back suction due to extreme solubility of gas in water.

Tests :—(i) When an aqueous solution of the acid is exposed to air, it turns brown due to separation of iodine by oxidation with atmospheric oxygen.

$$4HI + O_2 = 2H_2O + 2I_2$$

(ii) When the aqueous solution of hydroiodic acid is mixed with manganese dioxide and the mixture heated, violet vapour of iodine makes its appearance.

$$MnO_2 + 4HI = MnI_2 + I_2 + 2H_2O.$$

(iii) When silver nitrate solution is added to an aqueous solution of Hydroiodic acid a yellow precipitate of silver iodide, insoluble in conc. HNO_3 as also in NH_4OH, is obtained.

$$HI + AgNO_3 = AgI + HNO_3.$$

(iv) When chlorine-water and carbon disulphide are added to Hydroiodic acid solution and the mixture shaken and allowed to settle, violet carbon disulphide layer is obtained at the bottom of the test tube. The iodine liberated dissolves in CS_2 giving a violet solution.

$$2HI + Cl_2 = 2HCl + I_2$$

Q. 6. *State what happens when,*

(a) *A solution of cuprous chloride in Hydrochloric acid is shaken with air in a stoppered bottle,*

(b) *Ferrous sulphate solution acidified with sulphuric acid is treated with dilute hydrogen peroxide,*

(c) *The gas obtained by heating ammonium sulphate and sodium nitrate is led over strongly heated copper turnings.*

(d) *The gas obtained by roasting Iron Pyrites in air is passed through a solution of Ferric chloride almost neutral.*

Give equations.

Ans. (a) A solution of Cuprous chloride in Hydrochloric acid is colourless but when this solution is shaken with air in a stoppered bottle, it rapidly turns green due to oxidation into Cupric chloride by atmospheric oxygen.

$$2Cu_2Cl_2 + 4HCl + O_2 = 4CuCl_2 + 2H_2O.$$

(b) Ferrous sulphate solution acidified with sulphuric acid is green in colour. It is oxidised by dilute hydrogen peroxide to ferric sulphate solutions and the colour of the solutions turns brown..

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O.$$

(*c*) The gas obtained by heating ammonium sulphate and sodium nitrate together is nitrous oxide.

(i) $(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 4H_2O + 2N_2O.$

When this nitrous oxide is passed over strongly heated copper turnings, copper is oxidised to cupric oxide and nitrogen gas is liberated.

$$Cu + N_2O = CuO + N_2.$$

(d) The gas obtained by roasting Iron Pyrites in air is sulphur dioxide.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

When this sulphur dioxide is passed through an almost neutral solution of Ferric chloride, yellow in colour, ferric chloride is reduced to ferrous chloride and the solution turns colourless.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

Q. 7. *Write an essay on water, touching on the following points :—*

Kinds of water—their differences—hard and soft water—outlines of the general methods of softening—utility of softening—use of water in our daily life and industries—distilled water—ice—drinking water supply in town.

Ans. Natural water may be classified into four categories depending upon the amount of impurities present in them, viz.

(a) **Rain water** :—It is the purest form of natural water, being obtained by a process of distillation occurring in nature. But in passing through the atmosphere, rain water takes up from it many gases and vapours, *e.g.*, Oxygen, Nitrogen, Carbon dioxide, Nitrous and Nitric acids, Ammonia, Sulphur dioxide, etc., and also solid matter floating in the air. But after a heavy downpour, the rain-water collected is almost nearly pure water.

(b) **Spring (or deep-well) water** :—Rain-water, as it soaks into the ground, begins to dissolve more or less mineral matters —e.g., carbonates, chlorides, and sulphates of calcium, magnesium, potassium, sodium, and (often) iron, derived from the soil, and also carbon dioxide. It often contains sulphuretted hydrogen. Owing to natural filtration through porous strata this water is clear and practically free from suspended impurities when it finally comes out as spring.

(c) **River-water** :—Surface water as well as spring-water ultimately collect in rivers. River-water contains not only dissolved solids derived from the soil over which it flows, but also, owing to its great force, it carries along a large amount of insoluble matter, both organic and inorganic, in suspension. Hence it is generally turbid.

(d) **Sea-water** :—It contains the largest amount of dissolved salts, being fed by river-water, which carries all its dissolved solids and some portion of suspended matter into the sea. The dissolved salts usually consist of chlorides, sulphates, carbonates, bromides and iodides of sodium, potassium, calcium and magnesium, of which sodium chloride or common salt is the most important. Sea-water contains about 3·6% of total solids of which 2·6% is common salt. Hence it is the impurest form of natural waters.

Natural water may also be broadly divided into two kinds according to the nature and amount of dissolved substances, *viz.* (*a*) *Fresh water*, generally meaning thereby natural water that does not contain an excessive amount of dissolved impurity, *i.e.*, not to such an extent as to sensibly affect the taste : e.g., Rain-water, River-water, and ordinary spring or deep well water : (*b*) *Mineral water* which includes natural spring-water which has acquired a special taste, or a specific (medicinal or curative) property on account of an unusual amount of some particular substance or substances being held in solution ; e. g., water from springs at Bath and Harrogate in England, containing dissolved Hydrogen sulphide and possessing hepatic properties ; water from spring at Epsom in Germany containing dissolved magnesium sulphate *etc.* Water that readily forms lather with soap is called *soft* water, whilst water that does not produce a lather until much soap is consumed, is called *hard* water. Hardness of natural water is usually due to the presence of soluble calcium and magnesium salts dissolved in such water.

Hard water may be again of two types ; (*i*) *temporarily hard water*, which contains bicarbonates of calcium and magnesium dissolved in it ; (*ii*) permanently hard *water*, which contains chlorides and sulphates of calcium and magnesium dissolved in it.

Temporarily hard water can be softened by simple boiling, when insoluble calcium and magnesium carbonates are precipitated :—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

Temporary hardness is also removed by adding requisite quantity of slaked lime.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

Now on account of an appreciable solubility of magnesium carbonate, twice the requisite quantity of lime required for precipitating magnesium carbonate is to be added in order to precipitate magnesium as hydroxide, which is much less soluble than magnesium carbonate :

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2 + 2H_2O.$$

Permanently hard water can be softened by adding sodium carbonate (washing soda) to such water :—

$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Both temporary and permanent hardness can be removed by Gan's Permutit Process. Permutit is an artificial preparation consisting of sodium alumino-silicate. It has the capacity of exchanging bases. When hard water, containing salts of calcium and magnesium in solution, is filtered through a stratum of permutit, exchange of sodium for calcium and magnesium takes place. Sodium chloride and sulphate formed passes into water and renders water soft for sodium salts are without action on soap. Calcium and magnesium are retained as insoluble alumino-silicates on the filter-bed. When the permutit becomes exhausted, it is regenerated by being kept in contact with a strong solution of common salt.

Softening of water confers several advantages, viz. (i) When softened water is used as boiler-feed water, no "fur" is produced inside the boilers at the time of raising steam ; the deposit of fur causes a great waste of fuel and increases the wear and tear of the boiler-plates. (ii) On the other hand boiler-plates are not damaged by acids generated by hydrolytic decomposition like $MgCl_2 + H_2O = MgO + 2HCl$ when soft water is used in boilers. (iii) For washing purposes, use of soft water brings down the consumption of soap to a great extent.

Natural waters are used in our daily life : (1) for drinking purpose ; (2) for washing and other household purposes ; (3) for irrigation of lands in agriculture. In industries water is used (1) as a feed-water for boilers ; (2) in chemical works and factories as a cooling agent : (3) in the preparation of medicine. Besides, water is used as a solvent and in chemical analysis.

Distilled water is fairly pure water. It may be obtained in the laboratory by the method described in Q. 1, (*a*). Industrially it is obtained by using a copper boiler and a tin coil condenser. It is required for preparation of medicines, in chemical analysis and in storage battery.

Ice is water which has been solidified by cooling. Usually on a manufacturing scale water kept in a tank is cooled by circulation of liquid ammonia through coils set round the tank. Blocks of ice are thereby produced.

Drinking water to be supplied in Town is usually drawn from a river or specially preserved tank. Usually such water is first drawn into a tank and allowed to stand there for a time in contact with blocks of alum placed in iron cages in order that suspended impurities may mostly settle out. It is then discharged under pressure through iron pipes in the form of a short spout on the cemented inside-edge of the filter-bed. This brings about proper aeration and exposure to sunshine whereby germs are partially destroyed. Next water is passed through filter-beds consisting of layers of fine sand, coarse sand and gravel. The filtered water is collected in the channel.

Water for town supply is next sterilised by adding small

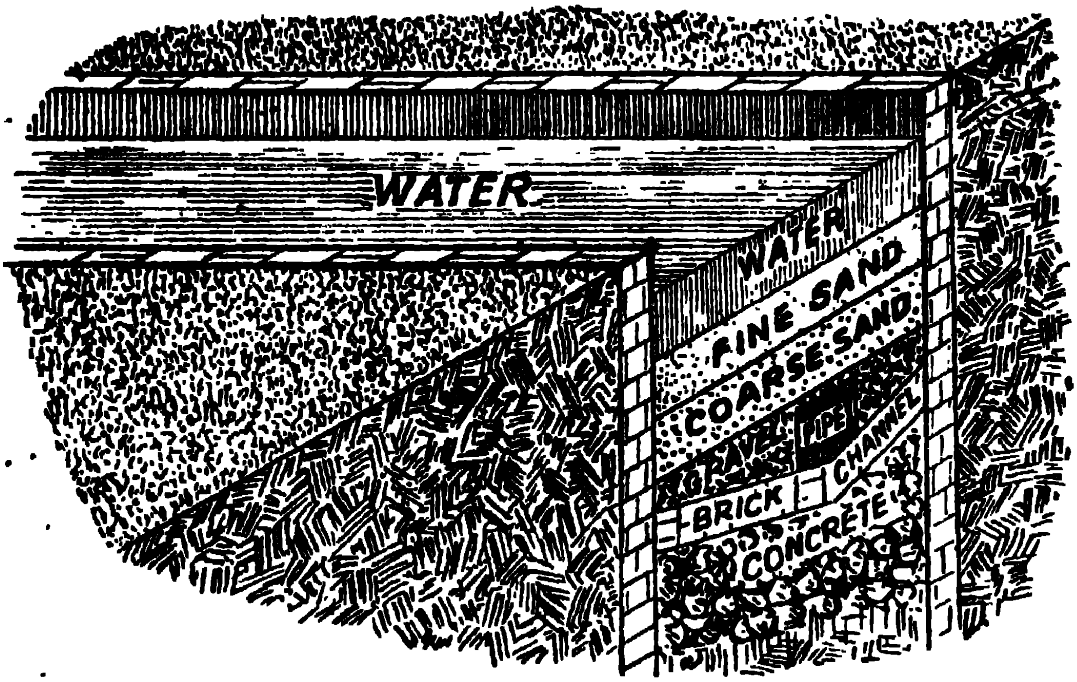


Fig. 127

quantities of chlorine or bleaching powder. In great cities Europe sterilisation is carried out by treatment with ozone.

SECOND PAPER

Q. 1. *State Faraday's laws of electrolysis and deduce the relationship between the chemical equivalent and the electrochemical equivalent of an element.*

The same current was passed through solutions of copper sulphate, silver nitrate, and dilute sulphuric acid for the same interval of time. If the volume of hydrogen liberated be 37·4 c.c at 750 mm. pressure and 27°C., and the amount of silver and copper deposited on the respective cathodes be 0·3267 gm. and 0·0954 gm. respectively, calculate the equivalent weights of silver and copper.

Faraday's laws of electrolysis :—These are two in number.

(a) The mass of an ion liberated during electrolysis is directly proportional to the strength of the current and to the time during which the current flows, *i.e.* to the quantity of electricity flowing through the circuit.

Thus, if W be the mass in grams of an ion liberated, C the strength of the current in ampere and t the time in second during which the current flows, $W \propto Ct$, or $W = ZCt$ where Z is a constant. Now when $C = 1$ amp. and $t = 1$ sec. then $W = Z =$ mass of ion liberated by unit quantity of electricity. This quantity Z is called the *electrochemical* equivalent of the substance.

(2) When the same quantity of electricity is passed through different electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.

(b) From the first law, we have $W = ZCt$; where W = the mass of an ion liberated by a current of C amperes flowing for t seconds, and Z is a constant. Now when $C = 1$ ampere, and $t = 1$ second, or when 1 coulomb of electricity is passed through the circuit, $W = Z$, which is a constant for any one element and is called the electro-chemical equivalent of the element.

Now from the second law, it follows that the electrochemical equivalents of substances are proportional to their chemical equivalents.

So we have the relationship,

$$\frac{\text{Electrochemical equivalent of a substance A}}{\text{Electrochemical equivalent of a substance B}} = \frac{\text{Chemical equivalent of A}}{\text{Chemical equivalent of B}}$$

$$\text{Hence, } \frac{\text{E. C. E. of any element}}{\text{E. C. E. of Hydrogen}} = \frac{\text{C. E. of the element}}{\text{C. E. of Hydrogen}}$$

$$= \text{C. E. of the element}$$

$$(\because \text{ C. E. of H} = 1).$$

$\therefore$ Electro-chemical Equivalent of any element = Electro-chemical Equivalent of Hydrogen × Chemical Equivalent of the element.

Let V c.c. be the volume of hydrogen at N.T.P., i.e., 0°C and 760 mm. pressure.

Then, by Boyle's and Charles' Laws, we have

$$\frac{37{\cdot}4 \times 750}{273+27} = \frac{V \times 760}{273+0}$$

$$\therefore \quad V = \frac{37{\cdot}4 \times 750 \times 273}{760 \times 300} \text{ c.c.}$$

$$= 33{\cdot}6 \text{ c.c.}$$

Since 1 c.c. of hydrogen at N. T. P. weighs 0·00009 gm.

∴ the weight of 33·6 c.c. of hydrogen at N. T. P.

$$= 33{\cdot}6 \times 0{\cdot}00009 \text{ gm.}$$

$$= 0{\cdot}003024 \text{ gm.}$$

Since, by definition, the equivalent weights of silver and copper are respectively those weights (expressed as a mere number since it is the ratio of two weights) of silver and copper which are liberated by the time in which 1 gm. of hydrogen is liberated,

$$\text{equivalent weight of silver} = \frac{0{\cdot}3267}{0{\cdot}003024} = 108{\cdot}03.$$

$$\text{and equivalent weight of copper} = \frac{0{\cdot}0954}{0{\cdot}003024} = 31{\cdot}54$$

Q. 2. (*a*) *Describe the preparation and properties of pure carbon monoxide. How is the formula of the gas established ?*

What volume of air at 27°C., and 750 mm. pressure would be required for the complete combustion of one litre of a gaseous mixture, containing equal parts of carbon monoxide and hydrogen by volume ?

Ans. Preparation of CO :—Conc. H_2SO_4 is taken in a flask fitted with a rubber cork through which pass a dropping funnel and a delivery tube. Sulphuric acid is then heated to about 100°C. and pure formic acid is added drop by drop from the dropping funnel to the hot sulphuric acid. As each drop of formic acid comes in contact with conc. H_2SO_4, the elements of water are abstracted from it and CO gas is evolved. The gas is collected by displacement of water.

$$H.COOH + H_2SO_4 = CO + [H_2SO_4 + H_2O].$$

Pure and dry specimen of the gas can be obtained by passing this CO first through a wash bottle containing concentrated H_2SO_4 and then collecting the gas by displacement of mercury.

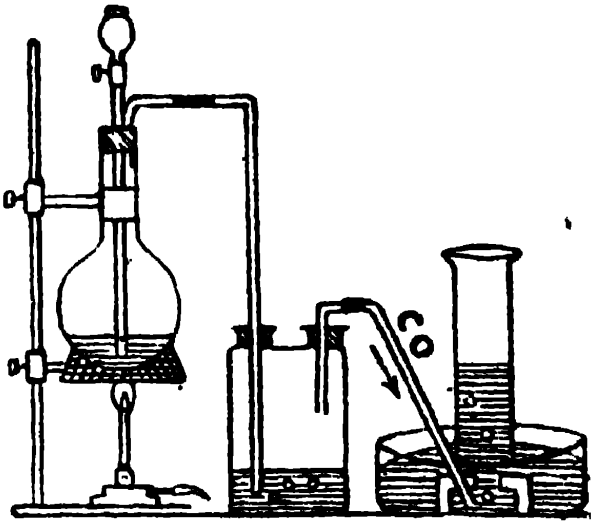


Fig. 128

Properties of Carbon monoxide. CO.—

Carbon monoxide is a colourless gas with a peculiar faint smell. It is slightly lighter than air and is practically insoluble in water. The gas is extremely poisonous ; it combines with the haemoglobin of blood forming *carboxy-haemoglobin* which is incapable of absorbing oxygen ; thus blood in the lungs loses its capacity of taking up oxygen and this brings about insensibility and ultimately death.

Carbon monoxide is a combustible gas. It burns with a characteristic lambent blue flame, forming CO_2, when ignited, $2CO + O_2 = 2CO_2$. An intimate mixture of carbon monoxide and oxygen, when inflammed, explodes violently.

It is a neutral oxide of carbon. It is an *unsaturated* compound and combines directly with chlorine, under the influence of sunlight with the formation of carbonyl chloride or *phosgene gas* : $CO + Cl_2 = COCl_2$. Finely divided nickel, cobalt and iron unite with carbon monoxide on heating, with the formation of a class of compounds called *carbonyls*, *e.g.*, nickel carbonyl $Ni(CO)_4$, iron carbonyl, $Fe(CO)_5$ etc.

Carbon monoxide is a powerful reducing agent at an elevated temperature. Thus, when carbon monoxide is passed over red-hot copper oxide, CuO is reduced to metallic copper and CO is oxidised to CO_2. $CuO + CO = Cu + CO_2$. Solid KOH when heated absorbs CO when passed into it under pressure forming potassium formate; $KOH + CO = HCOOK$. A solution of cuprous chloride in conc. HCl or in ammonia absorbs carbon monoxide, forming $CuCl,CO,2H_2O$.

Formula for carbon monoxide is obtained from a knowledge of its volumetric composition which is established in the following way:—

A few c.c. of pure and dry carbon monoxide is introduced into the closed limb of a U-shaped eudiometer tube, provided with a side-cock as shown in the adjoining figure, by the displacement of mercury. Next the level of mercury is brought to the same level in both tho limbs, and the volume of the gas is carefully read off. Let it be 30 c.c. Then an equal volume of oxygen is introduced into the closed limb of the apparatus, mercury level is adjusted to the same height in both the limbs and the volume of the mixture is carefully noted. It is found to be 60 c.c. The open limb of the tube is then closed with the thumb and a single electric spark is passed through the mixture by connecting the two Pt-wires sealed in the closed limb of the tube to the terminals of an induction coil. Carbon monoxide combines with oxygen with explosion to form carbon dioxide. The apparatus is allowd to cool, the mercury level is again adjusted to the same level in both the limbs and the volume of the gas remaining is carefully read off. It is found to be 45 c.c. The open limb of the tube is then completely filled up with mercury so as to exclude air; a piece of solid KOH is then placed on the surface of mercury, the mouth is closed with the thumb and by inverting the whole apparatus the solid KOH is introduced into the closed limb. Carbon dioxide is completely absorbed by KOH. The mercury level is again adjusted to the same height in both the limbs by letting out mercury through the side cock. The volume of the residual gas is noted carefully. It is found to be 15 c.c. That the residual gas is nothing but oxygen is proved by the facts that (*i*) it rekindles a glowing chip of wood, (*ii*) it

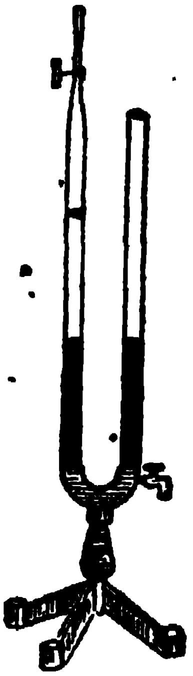


Fig. 127

forms brown fumes with nitric oxide (NO) and (*iii*) it is completely absorbed by alkaline pyrogallate.

From the data mentioned we find that 30 c.c. of carbon monoxide have combined with (30 − 15) or 15 c.c. of oxygen to produce (45 − 15) or 30 c.c. of carbon dioxide. Now, as carbon dioxide contains its own volume of oxygen, 30 c.c. of carbon dioxide contain 30 c.c. of oxygen. Now to produce these 30 c.c. of carbon dioxide, only 15 c.c. of oxygen—out of 30 c.c. added—have been used up. Therefore the remaining 15 c.c. of oxygen must have come from 30 c.c. of carbon monoxide ; or, 30 c.c. of carbon monoxide contain 15 c.c. of oxygen.

Thus it is proved that carbon monoxide contains half its volume of oxygen.

Hence, 2 vols. of carbon monoxide contain 1 vol. of oxygen.

Let *n* be the number of molecules present in 1 vol. of oxygen. Then, by Avogadro's hypothesis, 2*n* molecules of carbon monoxide contain *n* molecules of oxygen ;

Or, 2 molecules of carbon monoxide contain 1 molecule of oxygen or 2 atoms of oxygen, since oxygen molecule is diatomic. (Deduction of Avogadro's hypothesis).

Therefore, 1 molecule of carbon monoxide contains 1 atom of oxygen.

Hence the formula for carbon monoxide may be written as C_xO, where x is an integer and represents the number of carbon atoms present in a molecule of the gas. Now the density of carbon monoxide as determined experimentally = 14. Therefore the molecular weight of carbon monoxide = $14 \times 2 = 28$. That is to say, $12x + 16 = 28$, or $x = 1$.

Hence the formula for carbon monoxide is CO.

(*b*) The volume of gaseous mixture containing carbon monoxide and hydrogen is given to be 1 litre or 1000 c.c., but the temperature and pressure of the gas mixture have not been mentioned in the sum. The volume, therefore, is taken to be at N. T. P. Since carbon monoxide and hydrogen are present in equal parts by volume, therefore there are 500 c.c., each of CO and H_2 at N. T. P.

Now, from the equations

$$\begin{array}{llll} & 2CO & + \; O_2 & = 2CO_2 \\ & \text{2 vols.} & \text{1 vol.} & \\ \text{and} & 2H_2 & + \; O_2 & = 2H_2O \\ & \text{2 vols.} & \text{1 vol.} & \end{array}$$

We know that 2 vols. of CO require 1 vol. of O_2 and 2 vols. of H_2 require 1 vol. of O_2 respectively for their complete combustion, the gases being all measured at N. T. P.

Therefore, 500 c. c. of CO require 250 c.c. of O_2 and 500 c.c. of H_2 require 250 c.c. of O_2 for complete combustion, all gases being measured at N. T. P.

$\therefore$ the total volume of O_2 required for the complete combustion of the gas mixture measuring 1 litre at N. T. P. = (250 + 250) or 500 c.c. at N. T. P. Since air contains 21 per cent. of oxygen by volume, therefore total volume of air at N. T. P. required for complete combustion of the gaseous mixture $= \dfrac{500 \times 100}{21}$ c.c.

Let V c.c. be the volume of this air at 27°C and 750 mm. pressure. Then by Boyle's and Charles' Laws, we have

$$\frac{\dfrac{500 \times 100}{21} \times 760}{273 + 0} = \frac{V \times 750}{273 + 27}$$

$$\therefore \quad V = \frac{500 \times 100 \times 760 \times 300}{21 \times 273 \times 750} \text{ c.c.} = 2652 \text{ c.c.} = 2{\cdot}652 \text{ litres}$$

Q. 2. *Alternative :*

(*a*) *Describe the manufacture and the properties of white and red phosphorus. Explain how each form can be converted into the other.*

(*b*) *How may phosphorus pentoxide and phosphine be prepared from the element ?*

Ans. Manufacture of white phosphorus :—A mixture of powdered mineral phosphate, sand and coke is fed through a feed-hopper into a closed electric furnace made of brick work provided with an outlet above for the gases and phosphorus vapour, a slag hole below and carbon electrodes between which an electric arc is struck, producing a very high temperature.

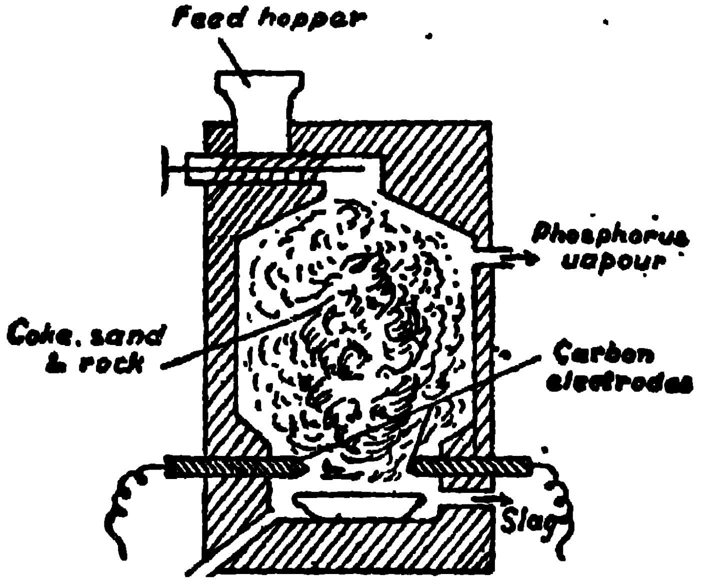


Fig. 130

The silica of the sand reacts with calcium phosphate producing calcium silicate and phosphorus pentoxide, P_2O_5,

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

The vapour of P_2O_5 is then reduced by carbon and carbon monoxide is formed and phosphorus is set free.

$$P_2O_5 + 5C = 2P + 5CO$$

Calcium silicate melts and sinks to the bottom, from where it is run off through the slag hole. Phosphorus vapours and CO escape through the outlet near the top and are passed into water where P_4 vapours condense. Fresh mixture is introduced and the process is continuous.

Manufacture of Red phosphorus.

Red phosphorus is prepared by heating white phosphorus in a covered cast iron vessel provided with a safety tube, out of contact with air, at a temp. of 240° – 250° in presence of a trace of iodine. The solid so obtained is first ground to powder with water and then boiled with caustic soda solution to remove any unchanged white phosphorus. It is then finally washed with water and dried.

White phosphorus is converted into red phosphorus when it is heated to 250°C. in an inert atmosphere in presence of a trace of iodine.

Red phosphorus, on the other hand, is converted into white-phosphorus by heating it in an inert atmosphere to above 550°C. until vapours are produced. By rapidly cooling the vapours white phosphorus is obtained.

(*b*). Phosphorus pentoxide is readily prepared by burning dry Phosphorus in a current of excess of dry air, when the pentoxide condenses as a voluminous powder known as Flower of Phosphorus.

$$4P + 5O_2 = 2P_2O_5.$$

Phosphine is prepared by heating white phosphorus with a concentrated solution of caustic soda or caustic potash in a flask from which air is displaced by coal gas.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Q. 3. *Describe the preparation and properties of the following and state their uses :—White lead, plaster of Paris, blue vitriol, minium and silica gel.*

Ans. *White lead.*—It is manufactured by the Dutch Process which gives the best product. Lead grids or perforated discs of lead are placed above a little vinegar in small earthenware pots. These pots are placed on the floor of a shed which is covered with spent tan-bark or horsedung. The pots are covered with wooden planks, on which are placed more of tan-bark or horse-dung and then similar pots. Successive layers of wooden planks and pots are placed one above the other until the shed is full. The whole is now allowed to stand for 6 to 10 weeks. During the time tan-bark or horsedung undergoes fermentation, which generates heat and carbon dioxide. Heat vaporises acetic acid which in presence of atmospheric oxygen and moisture attacks lead forming basic lead acetate. This basic acetate of lead is afterwards converted by CO_2 and heat generated by fermentation into basic lead carbonate, $2PbCO_3, Pb(OH)_2$, regenerating acetic acid. The pots are then taken out, the product is ground to powder to remove any unchanged lead, washed with water and dried.

$$2Pb + 2H_2O + O_2 = 2Pb(OH)_2$$

$$Pb(OH)_2 + 2CH_3COOH = Pb(CH_3COO)_2 + 2H_2O$$

$$2Pb(CH_3COO)_2 + Pb(OH)_2 = 2Pb(CH_3COO)_2, Pb(OH)_2$$

$$2Pb(CH_3COO)_2, Pb(OH)_2 + 2H_2O + 2CO_2 = 2PbCO_3, Pb(OH)_2 + 4CH_3COOH.$$

Properties.—White lead is amorphous white powder insoluble in water. On strong heating in contact with air it is converted into red lead, Pb_3O_4. It is turned black in town atmosphere on acconut of the presence of H_2S in town air. It is poisonous.

White lead is extensively employed as a pigment. It is also used in the manufacture of red lead and of flint glass.

Plaster of Paris—$2CaSO_4 . H_2O$. It is prepared by heating gypsum, $CaSO_4 . 2H_2O$ to a temperature not exceeding 120° in such a fashion that it does not come into contact with carbonaceous fuel to avoid reduction.

$$2CaSO_4,2H_2O = (CaSO_4)_2,H_2O + 3H_2O.$$

Properties :—Plaster of Paris is a white powder which forms a hard mass with water. This is known as setting of plaster of Paris. It is due to its hydration and conversion into Gypsum :

$$(CaSO_4)_2,\ H_2O + 3H_2O = 2(CaSO_4,\ 2H_2O).$$

On strong heating it loses all water and becomes *dead burnt* ; then it does not set with water.

$$(CaSO_4)_2,\ H_2O = 2CaSO_4 + H_2O.$$

Plaster of Paris is used for making moulds in pottery works, in surgical bandages, and in preparing busts, statues, etc.

Blue vitriol or copper sulphate pentahydrate, $CuSO_4$, $5H_2O$, can be obtained by heating metallic copper with conc. H_2SO_4, when SO_2 is evolved and copper sulphate remains in solution.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

After cooling, the solution is carefully decanted off and diluted and filtered. On crystallising the filtrate blue crystals of $CuSO_4$, $5H_2O$ are obtained.

It is manufactured by roasting copper pyrites, Cu_2S. Fe_2S_3. at such a temperature that Cu_2S is converted into $CuSO_4$ and Fe_2S_3 into Fe_2O_3. After cooling, the roasted mass is extracted with water. The solution is taken off, filtered, concentrated and cooled, when crystals of *blue vitriol*, $CuSO_4$. $5H_2O$, separate out.

Properties :—It is a blue, crystalline solid, crystallising with five molecules of water of crystallisation. On heating to 100°C. it loses 4 molecules of water and at about 230°C. it becomes anhydrous and a white powder of $CuSO_4$ is formed. The white solid turns blue on treatment with water. It is soluble in water. On strong heating the anhydrous $CuSO_4$ decomposes leaving black CuO and evolving SO_3.

$$CuSO_4 = CuO + SO_3.$$

Uses : Blue vitriol is used in electroplating, electrotyping and in some electric cells. It is used in dyeing industry. Because of its germicidal action it is used in medicine and in agriculture. A spray of mixture of copper sulphate and milk of lime is used for killing moulds and fungi in vines and in wheat etc. Anhydrous copper sulphate (white) is used for detecting small amounts of water present in organic liquids.

Minium or *Red lead* is obtained when lead carbonate or lead monoxide is subjected to prolonged heating in contact with air, at a temperature not exceeding 450°C.

$$6PbO + O_2 = 2Pb_3O_4.$$

Properties :—It is a scarlet, crystalline powder, insoluble in water. On heating it decomposes above 450°C. giving lead monoxide and oxygen $2Pb_3O_4 = 6PbO + O_2$. Dilute acids react with Pb_3O_4 giving a bivalent lead compound and leaves a residue of PbO_2. Conc. HCl and conc. H_2SO_4 react with Pb_3O_4 on heating evolving chlorine and oxygen respectively.

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O.$$
$$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + O_2 + 6H_2O.$$

Conc. HNO_3, however, reacts only to give $Pb(NO_3)_2$ and a residue of brown PbO_2.

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Silica gel : *Preparation* :—When sodium silicate solution is heated to 100°C. and mixed with HCl, a gelatinous ppt. of silica gel, SiO_2, H_2O, is obtained. On careful heating of the carefully collected precipitate silica gel is obtained in the solid state. *Properties* :—It is a hard, transparent solid, resembling bits of broken glass. It is insoluble in water, but solid powder has a remarkable power of absorbing moisture.

Uses :—It is used as a dehydrating agent ; for keeping balance cases, cupboards, etc. dry and for drying the blast of air used in blast-furnace operation in the extraction of iron.

Q. 3. *Alternative* :

Starting from sodium chloride, describe how you would prepare sodium sulphate, sodium carbonate, sodium hydroxide and metallic sodium. State the uses of these substances.

Ans. From sodium chloride, anhydrous sodium sulphate is prepared by heating solid sodium chloride with strong sulphuric acid to a high temperature.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The solid mass thus obtained is called *salt cake*, Na_2SO_4. When the salt cake is dissolved in water, and the solution after filtration is concentrated to crystallisation point and cooled, Glauber's salt or sodium sulphate decahydrate, $Na_2SO_4, 10H_2O$, crystallises out.

Uses :—Sodium sulphate is used for the manufacture of glass and in medicine as a purgative. In Leblanc's process for manufacture of washing soda, sodium sulphate is obtained as a bye-product.

From sodium chloride, sodium carbonate can be prepared either by using solid sodium chloride by Leblanc's process, but this process is now going to be obsolete and now-a-days sodium chloride solution or brine is employed in the ammonia-soda process or Solvay's process for the manufacture of sodium carbonate from sodium chloride and that process is described here.

This process is based upon the reaction between hydrogen ammonium carbonate, NH_4HCO_3 and a strong solution of sodium chloride, according to the equation

$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3.$$

The actual operation is carried out as follows :—

Carbon dioxide is passed into a solution of common salt (called brine) under moderate pressure after the brine is saturated with ammonia gas and cooled. Carbon dioxide first reacts with ammonia forming ammonium bicarbonate.

$$CO_2 + NH_3 + H_2O = NH_4HCO_3.$$

The bicarbonate of ammonium then reacts with sodium chloride forming sodium bicarbonate and ammonium chloride by double decomposition.

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

The above reaction is reversible and hence sodium chloride is partially converted into sodium bicarbonate. This sodium bicarbonate being sparingly soluble separates out, leaving the more soluble ammonium chloride in solution. The above reaction takes place most efficiently between 30°—40°C. Sodium bicarbonate separating out is collected and converted into normal sodium carbonate by calcination.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The raw materials necessary are : (i) Brine, obtained directly from salt-beds, (ii) Lime-stone for generating carbon dioxide, the lime left being used afterwards for recovering ammonia from residual ammonium chloride solution, (iii) Ammonia.

The manufacturing process consists of five operations :—

(1) Saturation of brine with ammonia in ammonia-absorbers fitted with cooling arrangement.

(2) Carbon dioxide treatment of ammoniated brine in Solvay's carbonating towers under a pressure of 1—2 atmospheres.

(3) Filtration of the bicarbonate separating in Solvay's tower in vacuum filters.

(4) Calcination of the bicarbonate of sodium in order to get normal sodium carbonate and carbon dioxide which can be used over again.

(5) Recovery of ammonia from ammonium chloride solution by heating with lime, this ammonia being used over again. About 2% of ammonia is lost during working of the process and this is to be replaced. Hence it is found to be a self-contained operation and the working of the process is less costly in comparison to Leblanc process.

Uses :—Sodium carbonate is largely used in the manufacture of caustic soda, soap and glass, as a detergent for washing garments and for softening hard water. It is also used as a reagent in the laboratory.

Caustic soda is now-a-days manufactured by the electrolytic process from sodium chloride solution and several types of diaphragm cells are employed in its manufacture. The Castner-Kellner process is described here with the diaphragm cell used by them. Brine is electrolysed in a rectangular vessel divided into three compartments by means of slate partitions. The partition do not actually touch the bottom of the vessel but dip into a layer of mercury which covers its floor. The two outer compartments are filled with *brine* and are fitted with stout carbon rods which serve as the *anodes*. The *cathode* is a bunch of iron rods suspended in the middle compartment containing water to which a little caustic soda has been added to make it a conductor. The layer of mercury is electrically connected with the iron rods. The whole vessel rests, on one side, upon an eccentric. The anodes are now connected together and then with the positive pole of a battery, while the cathode is connected with its negative pole. The mercury is eletrically connected to the iron cathode. On passing electric current, chlorine is evolved at the anodes and is led away by exit pipes (shown in the figure) for the manufacture of bleaching powder. Sodium is liberated on mercury serving as cathode in the outer compartments where it dissolves in mercury producing an amalgam. The amalgam is transferred to the middle compartment by giving a slow rocking movement to the whole vessel by the eccentric. Sodium reacts with water in that compartment producing caustic soda and hydrogen. Caustic soda solution is now taken out and is evaporated in iron vessels. The solid so obtained is finally melted down and cast into sticks, pellets or balls. $2Na + 2H_2O = 2NaOH + H_2$. Hydrogen escapes through the outlet at the top of the middle compartment.

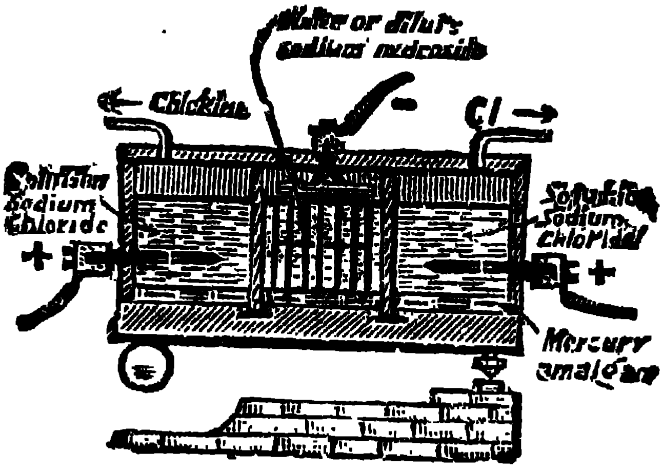


Fig. 131

Uses :—Sodium hydroxide is largely used in paper and textile industries, in dyeing, in refining oils, in the manufacture of hard soap, and for the preparation of metallic sodium. It is also used for the preparation of artificial silk, and as a laboratory reagent.

(*d*) Sodium is obtained from common salt by the electrolytic process as applied to fused common salt.

In the *Down's cell*, the operation is carried out by introducing sodium chloride or common salt mixed with sodium fluoride or $CaCl_2$ to lower its melting point through an opening *b* at the top and fused by heating. The carbon anode *a* is introduced through the base and is surrounded by a cylindrical iron cathode C. At the top of the anode there is a dome-shaped hood A for leading away the chlorine. The cathode is surrounded by an iron wire-gauze mantle at the top of which is a vertical pipe P communicating with a closed vessel R. Current is now passed through the molten electrolyte, when NaCl alone is decomposed but not NaF or $CaCl_2$. Chlorine evolved at the anode escapes through A, whereas sodium liberated at the cathode collects inside the mantle inverted over C. Gradually the level of sodium rises in the pipe P and ultimately it flows into the reservoir R.

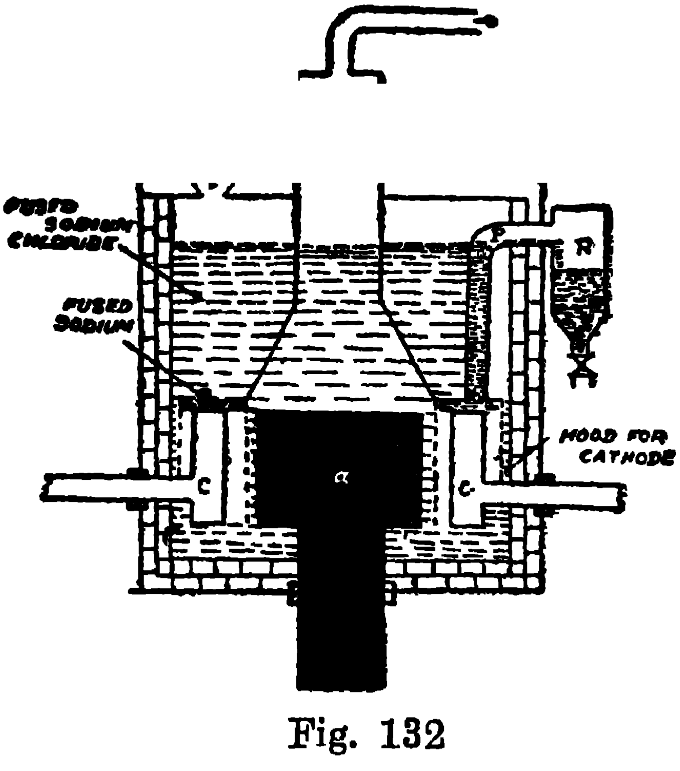


Fig. 132

Uses :—Metallic sodium is used in the preparation of sodium peroxide, sodium cyanide, in the manufacture of some organic compounds and as a reducing agent, particularly in the extraction of Magnesium, Aluminium, Boron and Silicon. Sodium in the form of wire is used for removing the last trace of water from alcohol and ether. An alloy of sodium and potassium is used in high-temperature thermometers. In Organic analysis, metallic sodium is used in the laboratory for the detection of different elements in Organic compounds.

Q. 4. *Describe the action of (a) air; (b) water, (c) dilute nitric acid, and (d) dilute sulphuric acid on the following metals : sodium, aluminium, iron and tin. Give equations where necessary.*

Ans. (*a*) *Action of air on*

Sodium :—Perfectly dry air has no action on sodium. Moist air containing carbon dioxide first tarnishes the fresh surface of sodium to a film of the monoxide, which now reacts with the moisture present in air giving sodium hydroxide, NaOH ; this NaOH absorbs atmospheric CO_2 yielding Na_2CO_3. When heated in air, sodium burns with a golden yellow flame, forming the monoxide and the peroxide.

$$4Na + O_2 = 2Na_2O.$$
$$2Na + O_2 = Na_2O_2.$$

Aluminium :—Dry air has no action on metallic aluminium ; moist air produces a thin coating of the oxide Al_2O_3 which protects the metal from further action. When strongly heated in air, aluminium burns brilliantly giving mainly Al_2O_3.

$$4Al + 3O_2 = 2Al_2O_3.$$

Iron :—Dry air has no action on iron at the ordinary temperature but it is converted by moist air and atmospheric carbon dioxide into *rust*, a hydrated oxide of iron, $Fe_2O_3.H_2O$. When heated to a high temperature it burns in oxygen of air brilliantly, throwing out sparks of Fe_3O_4.

$$3Fe + 2O_2 = Fe_3O_4.$$

Tin :—Dry air has no action on the metal. It also remains unchanged in moist air at the ordinary temperature, but it becomes covered with a thin crust of oxide when exposed to air in the fused condition. When heated to white heat in air, tin burns with a white light producing stannic oxide, SnO_2.

$$Sn + O_2 = SnO_2.$$

(*b*) *Action of water on* :—

Sodium :—Sodium decomposes water at the ordinary temperature, evolving hydrogen and forming sodium hydroxide in solution.

$$2Na + 2H_2O = 2NaOH + H_2.$$

Aluminium :—Aluminium powder or aluminium amalgam reacts with boiling water, evolving hydrogen as gas and forming insoluble aluminium hydroxide.

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2.$$

Iron :—When water in the form of steam is passed over red-hot iron, hydrogen is liberated as gas and ferrosoferric oxide is produced in the solid state.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Tin :—Tin does not react with water, particularly when both are pure.

(*c*) *Action of dilute nitric acid on* :—

Sodium :—Sodium reacts with dilute nitric acid forming sodium nitrate and evolving oxides of nitrogen and forming even a little ammonium nitrate.

Aluminium :—When metallic aluminium is placed in dilute nitric acid, the reaction starts slowly at first, but no gas is evolved and ultimately the reaction stops.

Iron :—Iron reacts with dilute nitric acid, forming a solution of ferrous nitrate and ammonium nitrate.

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 3H_2O + NH_4NO_3.$$

Tin :—When cold and dilute nitric acid reacts with tin, stannous nitrate and ammonium nitrate are formed in solution.

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

(*d*) *Action of dilute sulphuric acid on* :—

Sodium :—Sodium reacts with dilute sulphuric acid in the cold forming sodium sulphate and evolving hydrogen.

$$2Na + H_2SO_4 = Na_2SO_4 + H_2.$$

Aluminium :—Aluminium reacts with dilute sulphuric acid in the cold, forming aluminium sulphate in solution and evolving hydrogen as gas.

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2.$$

Iron :—Iron reacts with dilute sulphuric acid in the cold, forming ferrous sulphate in solution and evolving hydrogen as gas.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Tin :—Tin reacts only slowly with dilute sulphuric acid in the cold, giving stannous sulphate in solution and evolving hydrogen as gas.

$$Sn + H_2SO_4 = SnSO_4 + H_2.$$

Q. 4. *Alternative :—*

(i) *Compare the physical and chemical properties of the elements magnesium, calcium, and zinc, illustrating your answer with reference to their oxides, hydroxides and sulphates.*

(ii) *You are given a white powder, which may be an oxide of calcium, magnesium or zinc. Describe how you would proceed to identify the substance.*

Ans. (i) All these elements are white metals with densities, Mg 1·74, Ca 1·55 and Zn 7·1. They are all good conductors of heat and electricity. All these elements show uniform valency of 2 in their compounds. Magnesium and calcium are prepared by the electrolysis of their fused chlorides, whereas zinc is obtained by the reduction of its oxide by carbon.

Magnesium slowly tarnishes in air and burns in air to MgO and Mg_3N_2 and when heated decomposes steam ; calcium readily tarnishes in air and burns in air when heated to CaO and Ca_3N_2 and is capable of decomposing cold water ; zinc also slowly tarnishes in air and burns when strongly heated in air only to ZnO and when heated decomposes steam. All the three elements dissolve in dilute acids with the liberation of hydrogen. Magnesium gives rise to a very stable oxide, non-reducible at furnace temperature by C or hydrogen ; this oxide is a weak base and dissolves in 50,000 parts of water. Calcium forms a very stable oxide, also incapable of being reduced to metal by C or hydrogen ; this oxide is a strong base and dissolves in 400 parts of water. Zinc, on the other hand, forms a stable oxide, but this oxide can be reduced by carbon ; also this oxide is amphoteric in character and dissolves in ·250,000 parts of water. Magnesium forms a deliquescent solid chloride of the formula $MgCl_2, 6H_2O$ which is hydrolysed to MgO on ignition : $MgCl_2, 6H_2O = MgO + 2HCl + 5H_2O$. Calcium forms a chloride which is also a deliquescent solid, crystallising with 6 molecules of water ($CaCl_2, 6H_2O$). This chloride is only slightly hydrolysed on ignition. Zinc gives a deliquescent solid chloride, $ZnCl_2, H_2O$ which is hydrolysed to ZnO on ignition : $ZnCl_2, H_2O = ZnO + 2HCl$. Magnesium forms a sulphate, $MgSO_4, 7H_2O$ isomorphous with zinc sulphate $ZnSO_4, 7H_2O$. The sulphates of Mg and Zn dissolve in 4 parts and 0·75 parts of water respectively. Both of them form double salts of the type $(NH_4)_2SO_4, MgSO_4, 6H_2O$ and $K_2SO_4, ZnSO_4, 6H_2O$. Calcium on the other hand, forms a sulphate, $CaSO_4, 2H_2O$, sparingly soluble in water, 1 part dissolving in 400 parts of water.

(ii) (a) The oxide can be identified in the dry way by heating it on charcoal under the oxidising blowpipe flame, when it begins to glow. The residual white solid is then treated with a drop of cobalt nitrate solution and heated again under the oxidising blowpipe flame. If the residual mass is green, the orginal white powder is zinc oxide ; if the residual mass is pink, the original white powder is magnasium oxide ; when the residual mass is grey, the original white powder is calcium oxide.

(b) In the wet way the procedure for identification of the oxide is as follows :—

The oxide is dissolved in dilute HCl. The solution so obtained is treated with a little more HCl and heated to boiling. Through the boiling solution H_2S is passed in. No precipitate is formed. H_2S is then boiled off, a drop of HNO_3 added to it and the mixture heated to boiling. Then solid NH_4Cl and NH_4OH are added to the solution till the smell of ammonia persists. No precipitate appears at this stage on heating. Next H_2S is passed through the solution. If any white precipitate appears, then the oxide is of zinc. If no precipitate is formed at this stage, H_2S is boiled off and then NH_4OH and $(NH_4)_2CO_3$ added to the cooied solution. If any white precipitate is formed at this stage, then the original oxide is of calcium. If no precipitate is formed even now, to the clear solution disodium hydrogen phosphates is added and the mixture vigorously shaken and the side of the vessel is scratched with a glass rod. Appearance of white crystalline precipitate confirms that the original white powder is magnesium oxide.

Q. 5. *Name the principal mineral sources of iron. Describe briefly the blast-furnace process of manufacturing iron, explaining clearly the chemical reactions that occur inside the furnace.*

Give an account of the properties of cast iron, wrought iron and steel, stating the difference in their composition.

Starting from iron, describe the preparation of ferrous sulphate and ferric chloride.

Ans. The important mineral sources of iron are :

(1) Red haematite, Fe_2O_3
(2) Brown haematite or Limonite, $2Fe_2O_3, 3H_2O$
(3) Magnetite or Magnetic iron ore, Fe_3O_4
(4) Spathic iron ore or Siderite, $FeCO_3$.

Pig iron or *Cast iron* is manufactured from iron ores like haematite or spathic iron ore by the blast-furnace process.

The extraction consists of two operations, viz., (1) roasting the ore in air in order to drive off water and CO_2, so as to obtain porous ferric oxide, and (2) reducing the oxide with coke using lime-stone as a flux in the blast-furnace.

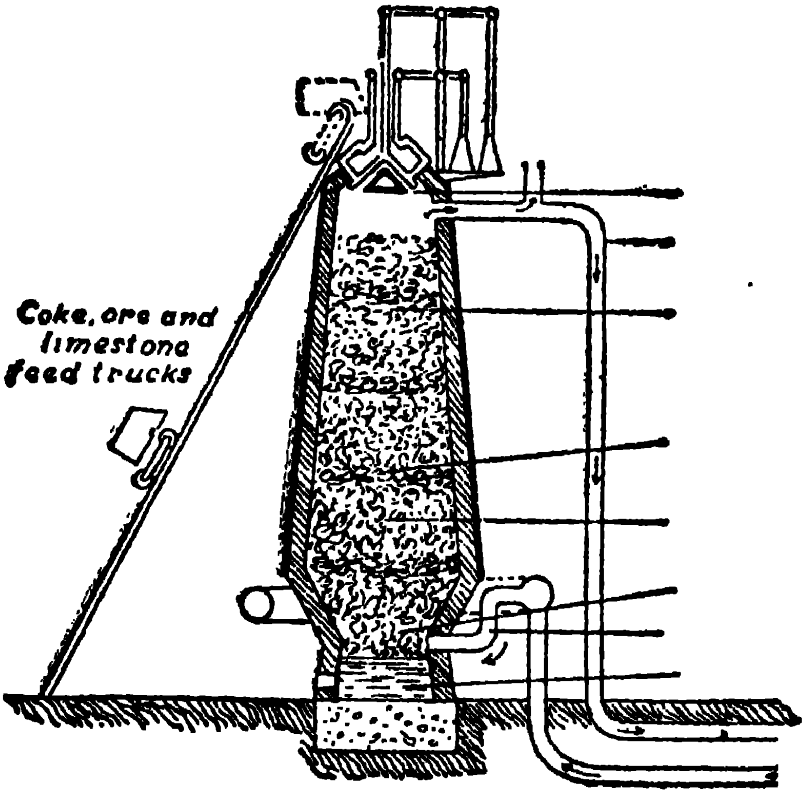


Fig. 133

A blast furnace is from 80 to 100 ft. high and 15 to 20 feet wide at the broadest part (Fig. 133). It is made of steel, and lined inside with fire bricks. The top of the furnace is closed by a *cup-and-cone arrangement* which can be opened or closed at will by means of a lever. There is a flue near the top for escape of hot gases from the furnace. Near the base of the furnace, hot and dry air at about 700° – 800°C. is forced in under pressure through water-cooled pipes called *tuyeres*. The blast of air is heated by passing through loose brick work (Cowper's stove) raised to a high temp. by combustion of waste gases drawn from the flue near the top of the furnace. The roasted ore, coke and limestone in right proportions are introduced into the furnace by lowering the cone. The furnace is first started by burning wood in the hearth of the furnace and feeding in coke only and turning on the blast at a slow rate. Ascending streams of carbon monoxide, formed by the action of air from the hot blast upon coke, reduces the descending oxide of iron to the metallic state. The following reactions take place :—

$$C + O_2 = CO_2$$
$$CaCO_3 = CaO + CO_2$$
$$CO_2 + C = 2CO$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$
$$CaO + SiO_2 = CaSiO_3$$

This reduction which is almost but never complete takes place near the top of the furnace where the temp. is about 500°C. The almost wholly reduced spongy mass of metallic iron gradually passes down the furnace, and becomes heated to a higher temperature, and finally, when the hottest part, just below the *boshes* (i. e., the widest part of the furnace), is reached where the temp. is about 1000°C., the iron is permeated by carbon obtained from the decomposition of carbon monoxide, gets itself completely reduced and combining with some amount of carbon forms cast iron and then it begins to melt, the melting point being much lower than that of pure iron.

Below this point the metal absorbs sulphur from the coke and phosphorus and silicon from the impurities present in the ore and limestone. Flowing down as it moves to the hearth, it completely melts and the molten mass runs down into the bottom, or the *hearth*. The limestone parts with the carbon dioxide, and the lime formed combines with the siliceous impurities (silica and alumina) present in the ore to form a fusible *slag* (calcium aluminium silicate). The lighter slag floats on the surface of the molten iron and protects it from the oxidising action of the blast. As the slag reaches a certain height, it runs out through certain openings known as *slag holes* and the molten iron is run off at suitable intervals through the *tap-hole* and allowed to flow into moulds of sand. Iron, thus obtained in the form of bars, is known as *pig-iron* or *cast-iron.*

By supplying fresh charges at the top and drawing off the slag and the metal through the slag hole and the tap-hole respectively near the bottom at regulated intervals, a blast-furnace once started goes on working days and nights, months and years without cessation until it requires repair or gets damaged beyond repair.

The main point of difference between pig-iron, steel and wrought iron is in their carbon content. Cast-iron contains the highest proportion of carbon, viz., 2 – 5%, steel contains 0·25 to 1·5% carbon whereas wrought iron is the purest form of commercial iron and contains only 0·12 to 0·25 per cent. of carbon. Besides cast-iron is the impurest form of commercial iron and it contains also S, P, Mn, Si, etc. as impurities. The main differences in properties of cast-iron, wrought iron and steel are tabulated below :—

Properties.	Cast Iron	Wrought Iron	Steel
1. Carbon content	2 – 5%	0·12 – 0·25%	0·25 – 1·5%
2. Impurities	Contains other impurties like Si, Mn, P, S, etc.	Purest form of commercial iron.	Intermediate in purity between Cast iron and Wrought iron, and contains intentionally added impurities like Ni, Cr, etc.

Properties	Cast Iron	Wrought Iron	Steel
3. Hardness	Hard	Soft	Hard and soft
4. Malleability	Brittle	Malleable	Malleable and brittle
5. Appearance	Crystalline	Fibrous	Crystalline
6. Tempering	Cannot be tempered	Can not be tempered	Can be tempered
7. Magnetisation	Cannot be permanently magnetised.	Cannot be permanently magnetised	Can be permanently magnetised

Ferrous sulphate from metallic iron :

Metallic iron is dissolved in dilute sulphuric acid, the solution is filtered and the filtered solution is concentrated by evaporation out of contact with air.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

On crystallisation, crystals having the composition $FeSO_4, 7H_2O$ separate out.

Ferric chloride from metallic iron :

Ferric chloride is known both in the *anhydrous* state ($FeCl_3$) and in the hydrated condition ($FeCl_3, 6H_2O$).

Anhydrous ferric chloride can be obtained from metallic iron by passing a current of dry chlorine over heated (900°—1000°C.) metallic iron in the form of wires taken in a hard glass tube which is connected to a receiver. Black $FeCl_3$ collects inside the receiver.

$$2Fe + 3Cl_2 = Fe_2Cl_6.$$

Hydrated ferric chloride is prepared by dissolving metallic iron in aqua regia, filtering the solution and then evaporating the filtered solution to crystallisation when yellow crystals of hydrated ferric chloride separate out. $HNO_3 + 3HCl = 2H_2O + NOCl + 2Cl$

nascent

$$Fe + 3Cl = FeCl_3.$$

nascent.

First Paper, 1957

Q. 1. *Explain and illustrate the following :—*

(*a*) *Allotropy*, (*b*) *equivalent weight*, (*c*) *valency*, (*d*) *atomic weight.*

Ans. (*a*) **Allotropy** :—The property possessed by certain elements to occur in two or more forms, differing in physical and to some extent in chemical properties, is known as Allotropy or Allotropism. The less common forms are called the allotropic modifications of the common form.

Thus carbon occurs in several forms in nature e.g., diamond, graphite, coal, coke, charcoal, lamp-black, gas-carbon etc. Of these charcoal and coal are the more common forms and diamond, graphite, etc., are called the allotropic modifications of charcoal and coal.

(*b*) *Chemical equivalent* or the equivalent weight of an element is that weight of it which combines with or displaces from a compound one part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine. It is a mere number, since it can be expressed as

$$\text{Chemical equivalent} = \frac{\text{wt. of the element in certain unit}}{\text{wt. of hydrogen displaced by or combined with the given wt. of the element in same unit.}}$$

Thus, 12 parts by wt. of Magnesium can displace 1 part by weight of hydrogen.

Hence 12 is the chemical equivalent of Mg.

In the case of a compound its chemical equivalent or equivalent is that weight of the compound which contains hydrogen equivalent of the active element present in the compound. Thus, in Na_2CO_3, 46 parts by wt. of Na are present in 106 parts by wt. of Na_2CO_3. But the hydrogen equivalent of sodium is 23. Hence the equivalent of sodium carbonate is $\frac{106}{46} \times 23$ or 53 parts by weight.

(*c*) Valency of an element is its combining capacity with other elements and is expressed as a number which indicates the number of hydrogen atoms or chlorine atoms with which one atom of the said element can combine.

Thus the valency of carbon is four, meaning thereby that one atom of carbon combines with four atoms of hydrogen. Similarly the valency of nitrogen is three, since its hydrogen compound is NH_3.

(*d*). The atomic weight of an element is a number expressing the relative weight of an atom of the element with respect to the weight of an atom of hydrogen. Thus, when we say that the atomic weight of chlorine is 35·5, we mean that the weight of one atom of chlorine is 35·5 times the weight of an atom hydrogen.

$$\text{Thus, } \frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of hydrogen}} = 35{\cdot}5.$$

Hydrogen was taken as the standard in expressing the atomic weights of elements in terms of its atomic weight, because it is the lightest element known. But the hydrogen standard of the atomic weights of elements, which was strongly advocated by Proust, was to be given up on account of several complications, and in its place oxygen with an atomic weight value 16·00 has been accepted as the standard of atomic weights. On that basis, when we speak of the atomic weight of chlorine to be 35·46, we mean

$$\frac{\text{wt. of 1 atom of chlorine}}{\text{wt. of 1 atom of oxygen}} \times 16 = 35{\cdot}46.$$

N. B. There is a slight difference in the atomic weight values of different elements on the hydrogen standard and on the oxygen standard, since on the basis of $O = 16$, $H = 1{\cdot}008$ and not 1, as it was used in the hydrogen standard of atomic weights.

Q. 2. *What are the sources of Iodine? Describe how it is manufactured and purified. State its use and its important chemical properties.*

Ans. The chief sources of iodine are :—(1) sea-weeds, particularly deep-sea-weeds which are drifted ashore during storms ; (2) Chile salt-petre or caliche', $NaNO_3$, which contains sodium iodate, $NaIO_3$, in very small amount as impurity ; (3) petroleum brine.

In France, Great Britain and Japan, iodine is obtained from sea-weed and for the purpose deep-sea-weeds (somewhat rich in iodine) which are drifted ashore due to storms are first collected and then dried. The dried weeds are next carefully burnt taking precautions, so that no iodine is lost by decomposition and volatilisation. The ash so obtained is called *kelp*. It contains alkali metal iodides together with chlorides, sulphates, carbonates, etc. This *kelp* is next lixiviated with water in iron tanks heated by steam and the solution concentrated in iron pans and allowed to crystallise. At this stage sulphates, chlorides, etc. of alkali metals crystallise out. The *mother-liquor*, obtained after removal of these crystallised products, containing the iodides of Na and K and a little bromide, etc. is mixed with H_2SO_4 when sulphur from sulphides present in solution separates out. This sulphur is allowed to settle and the clear liquid from the top is taken in iron stills having lead still-heads and provided with earthenware receivers called *aludels* or *udels*.

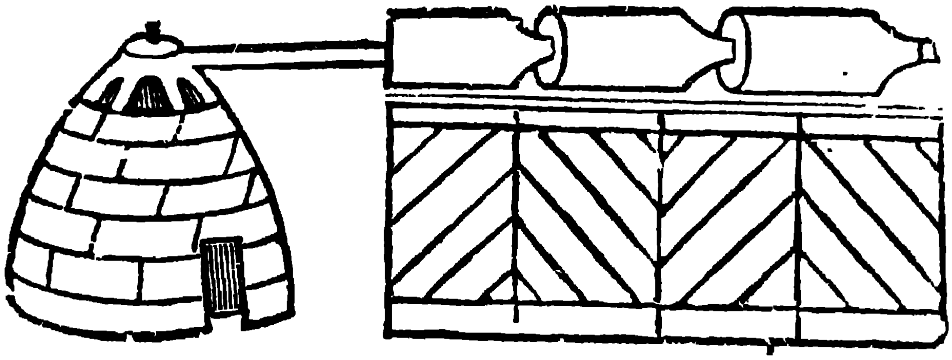


Fig. 134

In those iron stills the liquid is mixed with MnO_2 and conc. H_2SO_4 and heated, when iodine is liberated and sublimes off and collects inside the *aludels*.

$$2NaI + 3H_2SO_4 + MnO_2 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$$

The commercial product so obtained contains moisture, and free or combined chlorine or bromine. To get pure iodine, the commercial iodine is first ground with fresh lime (to remove moisture) and a little potassium iodide (to drive off chlorine and bromine). The mixture so obtained is then taken in a large-size beaker covered with a flask containing cold water. It is then heated when iodine sublimes and condenses on the bottom of the flask as fine, lustrous crystals.

Properties.—Iodine is a steel-grey solid having metallic lusture. It crystallizes in plates. The odour of iodine vapour is characteristic and it somewhat resembles that of chlorine. When heated quickly iodine sublimes, giving violet vapours. Upto 700°C. the density of iodine vapour corresponds to the molecular formula I_2. Above this temperature, the density gradually decreases until at 1700°C it becomes one half of its original value, showing thereby that dissociation into monatomic molecules is complete at this temperature.

$$I_2 \rightleftharpoons I + I.$$

Iodine is very slightly soluble in water. But it freely dissolves in organic solvents like chloroform, benzene and carbon disulphide giving *violet* solutions, and in alcohol and ether, giving *brown* solutions. It is very soluble in an aqueous solution of potassium iodide owing to the formation of potassium tri-iodide, KI_3. In this case also the colour of the solution is brown.

$$KI + I_2 \rightleftharpoons KI_3.$$

It combines directly with Hydrogen when the mixture of the two is passed over heated spongy platinum.

$$H_2 + I_2 = 2HI.$$

Iodine also combines directly with many metals like Na, Hg, etc., and also with many non-metals like P. It is the heaviest halogen known and as such its reactivity is found to be less than that of chlorine or bromine. It dissolves in cold and dilute KOH solution giving KI and KOI which is readily hydrolysed to hypoiodous acid HOI. With hot and strong

KOH solution. Iodine gives KI and KIO_3. $6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O$.

Iodine acts as a mild oxidising agent ; thus it oxidises H_2S to S.

$$I_2 + H_2S = 2HI + S.$$

It also oxidises SO_2 in presence of water to H_2SO_4

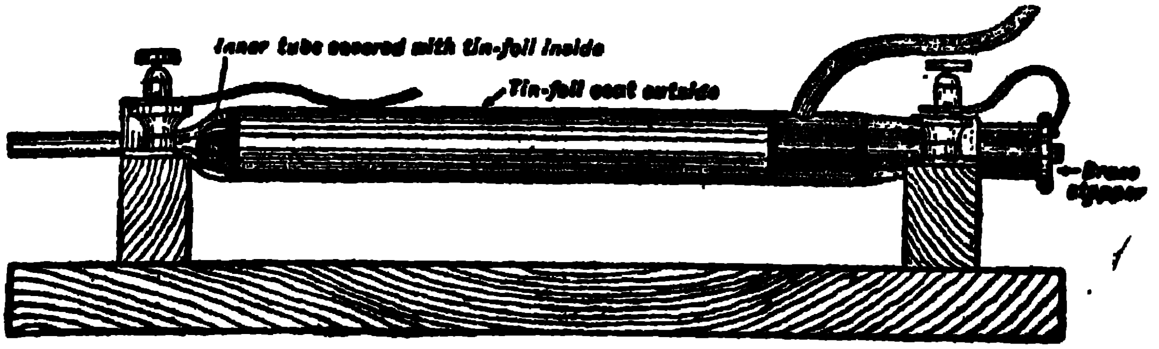
$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4.$$

It attacks the skin, possesses practically no bleaching properties and turns starch solution blue.

Uses. Iodine is used in medicine as *tincture of iodine* (used for reducing swellings and as a germicide) and internally in minute doses in cases of goitre. It is also used in the manufacture of dyes, iodoform, KI, NaI, AgI etc. It is also used in the laboratory in chemical analysis.

Q. 3. *Describe how ozone can be prepared and purified. State its use and how you would determine its composition.*

Ans. Ozone is most conveniently obtained in the laboratory in Siemen's Ozoniser by subjecting a stream of dry Oxygen to silent electric discharge. The Ozoniser consists of two concentric tubes, the inner tube is coated in the inner surface with tinfoil in metallic contact with one terminal ; the outer tube is coated on the outer surface with tinfoil in metallic contact with the other terminal. The two terminals are connected to an induction coil. A slow stream of dry O_2 is passed through the annular space between the concentric tubes and is exposed to the action of silent electric discharge. The gas coming out contains 3 to 8% of Ozone.



Siemens' ozoniser.

Fig. 135

Ozone can be purified by passing the ozonised oxygen through a U-tube immersed in liquid air, when a blue liquid is obtained. The pressure above the liquid is then reduced whereby the liquid separates into two layers. The lower layer is a solution of liquid oxygen in liquid ozone and by subjecting this layer to fractional evaporation, pure ozone is obtained.

Uses of ozone :—(1) The chief use of ozone is for sterilizing water and air. The drinking-water supply in some of the European cities is sterilized by treatment with ozone. The air of crowded rooms and of underground railways is purified by means of ozonised oxygen.

(2) Ozone is also used for bleaching oils, flour, starch, etc.

(3) It is now commercially employed for oxidation of organic compounds and of potassium manganate to potassium permanganate.

Composition of Ozone and its Chemical formula :—

This may be proved experimentally in the following manner : The contraction in volume on ozonising a known volume of oxygen is measured. The ozone is then absorbed by turpentine, and the further diminution in volume is noted. From these two data the composition of Ozone can be deduced and hence its molecular formula.

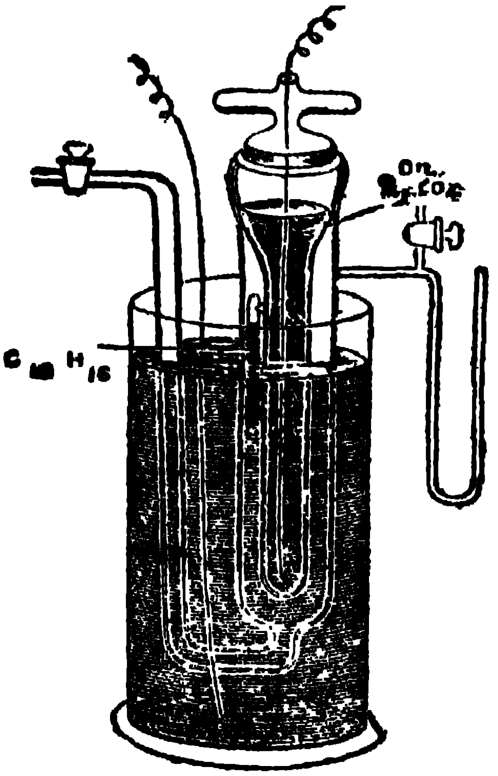


Fig. 136

The apparatus for studying these volume changes is shown in the adjoining figure. It is devised by Newth.

It consists of two concentric glass tubes, the inner tube fitted into the outer tube by a ground glass joint. The inner tube, which is nothing but an elongated hollow stopper, contains dilute H_2SO_4 and the apparatus, previously filled with dry oxygen, is placed in a jar of water and crushed ice. Two platinum wires are dipped into the two liquids, one in dilute H_2SO_4 in the hollow stopper, and the other in the jar containing iced water and are connected with the terminals of an induction coil. The turpentine is contained in a little sealed thin glass tube, almost capillary in bore, which is held in position between four little projecting glass points upon the hollow stopper and the outer tube. A manometer, containing concentrated sulphuric acid coloured with indigo, is in communication with the apparatus. The levels are adjusted, and the oxygen is ozonised by passing the electric discharge. A contraction in the volume results. When sufficient contraction has taken place, the discharge is interrupted, the apparatus is allowed to cool and the contraction is read off on the manometer gauge. The hollow stopper is then twisted, so as to break the tube of turpentine, and after absorption of ozone is complete, the further contraction is read off.

Experimental Results :

1st contraction on ozonisation $= x$ c.c.
2nd contraction on absorption of
Ozone by turpentine $= 2x$ c c.
$\therefore$ total diminution in volume of
Oxygen at the end of the experiment $= 3x$ c. c.

And the volume of Ozone formed $= 2x$ c. c.

Hence we conclude that 3 vols. of oxygen condense to give 2 vols. of ozone.

Let n be the number of molecules present in one volume of ozone. Then, by Avogadro's hypothesis, we get 3n molecules of oxygen condense into 2n molecules of ozone.

Or, 3 molecules or 6 atoms of oxygen condense into 2 molecules of ozone, since oxygen molecule is diatomic.

Hence the molecule of ozone consists of 3 atoms of oxygen and its formula is O_3.

Q. 4. *State Avogadro's hypothesis. Discuss how it has proved very useful in the determination of the atomic and molecular weight of gases.*

Ans. Avogadro's Hypothesis or Law :—Equal volumes of all gases, whether elementary or compound, contain identical number of molecules under the same conditions of temperature and pressure.

From Avogadro's hypothesis it is deduced that the molecular weight of any gas is twice its vapour density. So from determination of the vapour density of gases their molecular weights can be calculated. Determination of vapour density of gases is carried out by Dumas' method from the relation $\text{Density} = \frac{\text{wt. of V vols. of the gas}}{\text{wt. of V vols. of } H_2}$ the volumes being measured at the same temperature and pressure. Next, atomic weight of an element being the smallest weight of it found in the molecular weight of any of its compounds, the determination of the molecular weights of several gaseous compounds of the element and the subsequent determination, by analysis, of the amounts of the element present in molecular weights of those gaseous compounds, help in finding out the atomic weight of the element in question. Thus, in case of the gaseous element nitrogen, several gaseous compounds of the element are taken, *e.g.*, nitrous oxide, nitric oxide, ammonia. The vapour densities of the compounds are experimentally determined and next their molecular weights are calculated from the relation $M = 2D$. Then, by analysis, the percentages of nitrogen present in those compounds are found out and by calculation the amounts of nitrogen present in molecular weights of those gaseous compounds are calculated. From the numbers so found out, the smallest one is chosen to be the atomic weight of nitrogen. This procedure is tabulated below :—

Compound	Vapour density (Expt.)	Molecular weight (Calc.)	Percentage of nitrogen (Expt.)	Amount of N, present in molecular weight (Calc.)
Nitrous oxide	22	44	63·6	28
Nitric oxide	15	30	46·6	14
Ammonia	8·5	17	82·35	14

Thus 14, being the smallest weight of nitrogen found in the molecular weights of its several gaseous compounds, is accepted as its atomic weight.

Thus Avogadro's hypothesis has proved very useful in the determination of the molecular and atomic weights of gases.

Q. 5. *How would you distinguish (a) nitrogen peroxide from bromine vapour, (b) Cl_2 from SO_2, (c) O_2 from O_3 and (d) N_2O from NO? Give two tests in each case.*

Ans. (*a*) (*i*) When passed into water, nitrogen peroxide, a reddish-brown gas, dissolves forming a *colourless* solution. The solution contains nitric and nitrous acids and so it turns blue litmus paper red.

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

Bromine vapour, which is also reddish-brown in colour, dissolves in water, giving an *orange* solution which bleaches the colour of blue litmus paper.

(*ii*) When nitrogen peroxide is passed over heated metallic copper, nitrogen gas is set free which can be collected by displacement of water by making suitable arrangement for the same.

$$4Cu + 2NO_2 = 4CuO + N_2.$$

When bromine vapour is passed over heated metallic copper, no gas is set free ; only cupric bromide (a green solid) is formed.

$$Cu + Br_2 = CuBr_2.$$

(*b*) (*i*) When Cl_2 is passed into $KMnO_4$ solution, acidified with H_2SO_4, for a time, the purple colour of the permanganate solution is not discharged. But when SO_2 is passed into $KMnO_4$ solution, acidified with H_2SO_4, the purple colour is discharged due to the formation of manganous sulphate and potassium sulphate by reduction.

$$\begin{aligned}&2KMnO_4 + 5SO_2 + 2H_2O\\&\quad = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.\end{aligned}$$

(*ii*) When passed into water, Cl_2 gives rise to a greenish-yellow solution (chlorine water). SO_2, on the other hand, gives rise to a colourless solution.

Also, colour and smell may be made the basis of distinction of the two gases.

(*c*) (*i*) Oxygen is passed into potassium iodide solution acidified with H_2SO_4, when no iodine is liberated and the solution remains colourless as at the start. But on passing O_3 into acidified KI solution, iodine is liberated, turning the solution brown.

$$2KI + O_3 + H_2SO_4 = K_2SO_4 + H_2O + I_2 + O_2.$$

(*ii*) A filter paper is soaked in lead acetate solution and is next held before a current of H_2S issuing from a Kipp's apparatus. Black lead sulphide is thus formed on the filter paper. A current of O_2 is then passed over the blackened filter paper. No change in colour takes place even after a long time. Next a current of O_3 is passed over the black lead sulphide on the filter paper. The black colour changes to white due to the formation of $PbSO_4$ by oxidation of PbS.

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

(*d*) (*i*) When a jar of N_2O is exposed to air, no change is observed, but when a jar of NO is exposed to air, brown fumes of NO_2 at once appear.

$$2NO + O_2 = 2NO_2.$$

(*ii*) A glowing chip of wood is introduced into a jar of N_2O ; it bursts into flame ; but when introduced into a jar of NO, the glow is extinguished.

Also N_2O and NO can be distinguished by inverting the jars containing the two gases respectively over a trough of cold water, when N_2O alone will pass into solution and water will gradually rise in the jar containing it ; NO is insoluble in water and so no water will rise in the jar containing NO.

Q. 6. *Describe how you would prepare hydrogen fluoride and dry it. State its use and important chemical properties.*

Ans. Aqueous solution of hydrofluoric acid can be obtained by mixing powdered fluorspar (CaF_2) with conc. H_2SO_4 and then gently warming the mixture in a *lead retort*, when HF vapour is given off. The gaseous acid is then passed into water contained in *lead bottles*. The aqueous hydrofluoric acid so obtained is sent into the market in gutta-percha bottles.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Anhydrous hydrofluoric acid is prepared from potassium hydrogen fluoride KHF_2, called *Fremy's* salt. This substance is prepared from aqueous HF. For the purpose the aqueous solution of HF is divided into two parts. One portion is neutralised with K_2CO_3 and other portion is added to. the neutral liquid. The liquid is then evaporated in a Pt-dish, when crystals of Fremy's salt, KHF_2, are obtained. These crystals are first dried thoroughly before it can be used for preparing anhydrous HF. Thoroughly dried KHF_2, is taken in a platinum retort, connected with a platinum U-tube by means of a long platinum tube, The tubes are kept immersed in a freezing mixture of salt and ice. The retort is next heated when KHF_2 first melts and then decomposes giving off HF (boiling point 19·5°C). This HF condenses to a liquid in platinum U-tube.

$$KHF_2 = KF + HF.$$

The liquid is taken out and electric current is applied to it. So long as there is any moisture current flows and water decomposes evolving hydrogen and oxygen. As soon as the acid becomes perfectly anhydrous, the flow of current stops and electrical connections are removed and perfectly anhydrous HF is bottled in gutta-percha bottles.

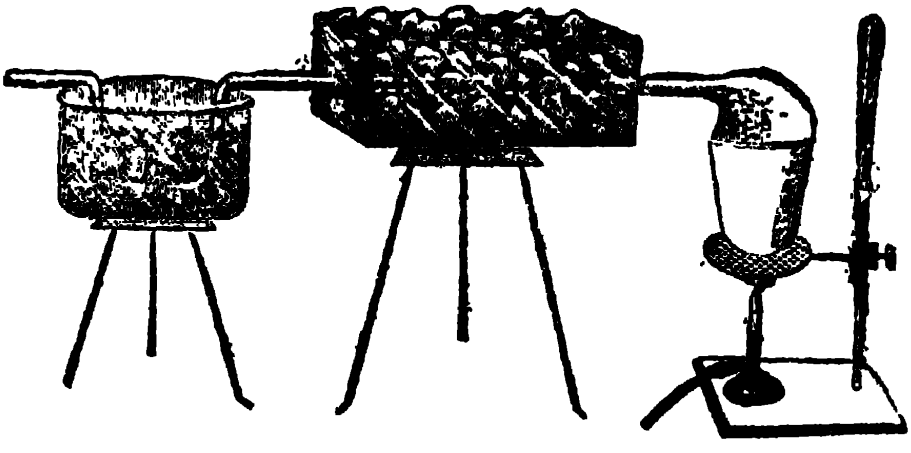


Fig. 137

Thus we have seen that in the preparation of aqueous HF *lead vessels* are employed, but in the preparation of *anhydrous* acid *platinum vessels* are employed.

Uses of HF :—Hydrofluoric acid is used for etching designs on glass. On account of its sterilising properties, it is used for sterilising casks of wines as also for destroying wild yeast in the brewing industry. It is also employed for removing silica from iron castings, for boring holes in petroleum mines and as an analytical reagent in the laboratory.

Important chemical properties :—

The acid is highly corrosive. It attacks many metals. Metals like sodium and potassium dissolve in the pure acid with the formation of their fluorides and evolution of hydrogen.

$$2K + 2HF = 2KF + H_2.$$

Silver and copper dissolves in the aqueous solution of the acid. The acid dissolves silica (SiO_2) with the production of silicon tetrafluoride and water :

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

This is the reason why hydrogen fluoride corrodes glass and porcelain which consist of silicates.

The acid also attacks organic substances like cotton, silk, gums, etc.

Q. 7. *State what happens, when bromine is added (a) to a solution of hot KOH, (b) to a solution of ferrous sulphate ; when (c) SO_2 is mixed with moist H_2S and (d) SO_2 is passed through a solution of $KMnO_4$. Give equations for the above reactions.*

Ans. (*a*) Bromine reacts with hot KOH solution forming potassium bromate and potassium bromide in solution.

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

The alkaline reaction of the solution is destroyed.

(*b*) Ferrous sulphate is oxidised by bromine in aqueous solution into ferric sulphate and at the same time ferric bromide is formed. Both the ferric salts remain in aqueous solution. So the colour of the solution changes from green to yellow.

$$6FeSO_4 + 3Br_2 = 2Fe_2(SO_4)_3 + 2FeBr_3.$$

(*c*) SO_2 oxidises H_2S to sulphur and is itself reduced to sulphur. So sulphur is deposited as a yellow solid.

$$2H_2S + SO_2 = 2H_2O + 3S.$$

(*d*) The purple colour of permanganate solution is destroyed, SO_2 reduces $KMnO_4$ to manganous sulphate and potassium sulphate and sulphuric acid is produced in solution by the oxidation of SO_2 by $KMnO_4$.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Q. 8. *What are the sources of phosphorus ? How is it* *manufactured? What are its allotropic forms? State their use and properties.*

Ans. Sources from which phosphorus is obtained are: (*i*) naturally occurring phosphatic rock, *phosphorite*, $Ca_3(PO_4)_2$ and (*ii*) calcium phosphate contained in bones. There are also many other compounds of phosphorus occurring in nature, such as *fluor-apatite*, $3Ca_3(PO_4)_2 . CaF_2$; *chlor-apatite*, $3Ca_3(PO_4)_2, CaCl_2$; *vivianite*, $Fe_3(PO_4)_2, 8H_2O$, etc., but none of them are employed as sources of phosphorus.

Manufacture of yellow phosphorus from bone-ash:—Bone-ash mainly consists of calcium phosphate (80%) and is utilised for getting yellow phosphorus. The old *Retort Process* is now obsolete and the modern *Electrical Process*, devised by Readman, Parker and Robinson, is now in vogue for getting yellow phosphorus.

A mixture of bone-ash, sand and coke is fed through the hopper, by a worm conveyer into a closed electric furnace which is made of brick-work. The furnace is provided with an outlet near the top for the escape of hot gases and vapours of phosphorus and another at the bottom for taking out the slag. Electric current is supplied through two stout carbon rods fixed

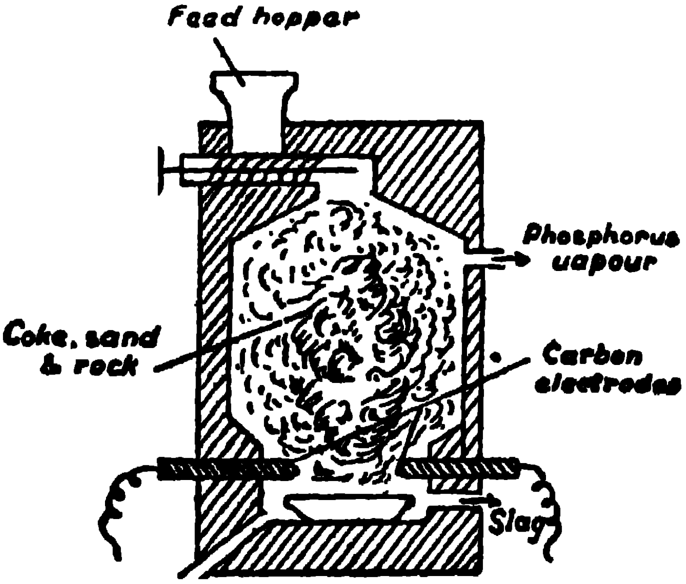


Fig. 138

a little above the bottom level as shown in the figure so as to form an "arc" inside the mixture which is heated very strongly in this way to about 1200° – 1500°C.

At the high temperature produced inside the mixture calcium phosphate reacts with silica, producing calcium silicate and phosphorus pentoxide.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$

Phosphorus pentoxide is then reduced by carbon of coke and phosphorus is set free.

$$2P_2O_5 + 10C = 10CO + 4P.$$

Calcium silicate melts and sinks to the bottom and therefrom it is run off by the slag-hole. Phosphorus vapours along with CO escape through the outlet near the top, and are passed into water, where phosphorus vapours condense into solid yellow phosphorus and carbon monoxide, being insoluble, escapes as gas.

Fresh mixture is introduced from time to time and the process is thus made continuous.

Phosphorus exists in different allotropic forms of which the two most important are : (*a*) White phosphorus and (*b*) Red phosphorus ; other allotropes are : (*i*) Scarlet phosphorus, (*ii*) Black phosphorus and (*iii*) Violet phosphorus.

Uses :—Phosphorus is largely used in the manufacture of matches. The head of the common *lucifer match* is composed of *white* P, mixed with KNO_3 or some other oxidising agent. Such matches are now-a-days supplanted by *safety matches*, the heads of which contain oxidising agents but no phosphorus. These ignite when rubbed on a surface coated with *red* phosphorus.

White phosphorus is also used in the preparation of P_2O_5 and of red phosphorus. Red phosphorus again is used in the laboratory for the preparation of HBr and HI as also in the preparation of phosphoric acid. A little amount is also used in making phosphor bronze, and as a rat-poison.

Properties of yellow and red phosphorus :—

Property	Yellow P	Red P
1. Colour.	Almost colourless.	Violet red.
2. Smell.	Garlic smell.	Odourless.
3. Specific gravity.	1·83	2·05 – 2·39
4. Melting point.	44°C.	500° – 600°C.
5. Action of CS_2 chloroform etc.	Readily soluble.	Insoluble.
6. Reaction when exposed to air.	Phosphoresces with glow and oxidation.	Does not phosphoresce (there is no glow and no oxidation).
7. Ignition temp.	30°C.	240°C.
8. Hot NaOH sol.	Readily reacts with hot NaOH sol. giving off PH_3	No action.
9. Chemical activity	Highly active.	Less active than yellow P
10. Physiological action.	Highly poisonous.	Not poisonous.
11. Stability.	Less stable at ordinary temperature.	Stable at ordinary temperature.

SECOND PAPER

Q. 1. *How would you obtain a pure specimen of silver nitrate from silver coin? What happens when a solution of silver nitrate is treated with (a) Caustic soda, (b) potassium cyanide, (c) ammonium hydroxide? Give equations.*

When one litre of a solution of silver nitrate was electrolysed for sometime 0·1259 gm. of the metal was deposited on the cathode. 20 c.c. of the solution gave 1·677 gms. of silver chloride after electrolysis. Find the strength of the solution in terms of normality before and after electrolysis.

(Ag – 108, Cl – 35·5).

Ans. Silver coin is made up of an alloy of silver and copper. Moderately dilute HNO_3 is added to a silver coin placed in a conical flask and the acid is warmed a little if necessary. The solution, green in colour due to $Cu(NO_3)_2$ produced from copper in the coin, is poured in a porcelain basin and evaporated to the crystallisation point and cooled. Crystals of $AgNO_3$ and $Cu(NO_3)_2$ are deposited together. These are collected and dried and then heated for a time in a basin by placing it in air-oven maintained at 250°C. At that temperature copper nitrate is decomposed into CuO (a black solid), N_2O_4 and O_2 (evolved away as gases), but silver nitrate does not undergo any decomposition,

$$2Cu(NO_3)_2 = 2CuO + 2N_2O_4 + O_2.$$

The residue is cooled and treated with water by stirring. The mixture is then filtered and the filtrate evaporated to crystallisation when, on cooling, pure crystals of silver nitrate are deposited. These are collected by filtration.

(*a*) When caustic soda is added to silver nitrate solution, silver oxide is precipitated as a greyish-black powder.

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O.$$

(*b*) When potassium cyanide is added to silver nitrate solution, at first a curdy-white precipitate of silver cyanide is formed, but on adding excess of potassium cyanide, the precipitate dissolves with the production of a complex salt, potassium argento-cyanide, and a clear solution is produced.

$$AgNO_3 + KCN = AgCN + KNO_3$$

$$KCN + AgCN = K[Ag(CN)_2]$$

(*c*) On adding ammonium hydroxide to silver nitrate solution, a transient precipitate of silver oxide appears, but it disappears as soon as it is formed. The solution then contains sliver-ammine nitrate.

$$2AgNO_3 + 2NH_4OH = Ag_2O + 2NH_4NO_3 + H_2O.$$
$$AgNO_3 + 2NH_4OH = [Ag(NH_3)_2]NO_3 + 2H_2O.$$

The molecular weight of silver chloride, AgCl, is 108 + 35·5 or 143·5, in which silver present is 108. Therefore, in 1·677 grams of silver chloride, silver present is $\frac{1·677 \times 108}{143·5}$ grams or 1·2621 grams. And this amount of silver is present in 20 c.c. of the solution given after electrolysis. Hence, in 1000 c.c. of the solution, after electrolysis, the amount of silver present = $\frac{1·2621 \times 1000}{20}$ grams = 63·105 grams. Now normal solution of silver nitrate is that which will contain 108 grams (one gram-equivalent) of silver. Hence the normality of the solution after electrolysis = $\frac{63·105}{108}$ N = 0·5843N. Before electrolysis, since from a litre of the solution, by electrolysis, 0·1259 gram of silver was deposited, the solution contained (63·105 + 0·1259) or 63·2309 grams of silver per litre of solution.

Hence, before electrolysis, the normality of the solution = $\frac{63·2309}{108}$N = 0·58547N.

Q. 2. *Make a comparative study of properties of marsh gas, ethylene and acetylene. How will you prepare a pure sample of each ? How will you separate methane from the mixture ?*

Ans. The comparative properties of the gaseous hydrocarbons are tabulated below :—

Properties	Marsh gas or Methane	Ethylene	Acetylene
1. Colour	Colourless	Colourless	Colourless
2. Odour	Odourless	Sweet odour	Sweet odour, when pure. Impure gas possesses an offensive smell.

Properties	Marsh gas or Methane	Ethylene	Acetylene
3. Solubility	Sparingly soluble in water.	Slightly soluble in water.	Soluble in water to the extent of 1 vol. of gas to 1 vol. of water.
4. Density	Much lighter than air (D=8).	Nearly as heavy as air (D=14).	Slightly lighter than air (D=13).
5. Nature	A saturated compound and so gives substitution products with the halogens. CH_4+Cl_2 $=CH_3Cl+HCl$.	An unsaturated compound and so yields additive products with the halogens. $C_2H_4+Cl_2$ $=C_2H_4Cl_2$.	An unsaturated compound and so gives additive compounds with the halogens. $C_2H_2+2Br_2$ $=C_2H_2Br_4$.
6. When set fire to in contact with air.	Burns with a scarcely visible blue flame.	Burns with a luminous flame.	Burns with a highly luminous and smoky flame.
7. Behaviour on admixture with oxygen and ignition	Explodes violently when admixed with twice its vol. of oxygen and ignited, CH_4+2O_2 $=CO_2+2H_2O$.	Explodes violently when mixed with thrice its volume of O_2 and fired. $C_2H_4+3O_2$ $=2CO_2+2H_2O$.	Explodes violently when mixed with two-and-a-half times its volume of O_2 and fired. $2C_2H_2+5O_2$ $=4CO_2+2H_2O$.
8. Reaction with chlorine	Reacts with chlorine in diffused light giving rise to several substitution products. CH_4+Cl_2 $=CH_3Cl+HCl$. CH_3Cl+Cl_2 $=CH_2Cl_2+HCl$ $CH_2Cl_2+Cl_2$ $=CHCl_3+HCl$. $CHCl_3+Cl_2$ $=CCl_4+HCl$. But in direct sunlight carbon separates as soot CH_4+2Cl_2 $=C+4HCl$.	Combines with chlorine readily giving an additive compound. $C_2H_4+Cl_2$ $=C_2H_4Cl_2$ But on being mixed with twice its volume of chlorine and ignited, carbon separates as soot and HCl is formed. $C_2H_4+2Cl_2$ $=2C+4HCl$.	Combines with chlorine only when it is in solution in S_2Cl_2, giving an additive compound. $C_2H_2+2Cl_2$ $=C_2H_2Cl_4$. But when it is brought into contact with Cl_2, it bursts into flame, giving HCl and depositing carbon. $C_2H_2+Cl_2$ $=2HCl+2C$.

Pure marsh gas is prepared by dropping water on aluminium carbide, passing the gas evolved first through an ammoniacal solution of cuprous chloride and then through a wash-bottle containing conc. H_2SO_4. The pure gas is collected by displacement of mercury.

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Pure ethylene is prepared by heating carefully a mixture of 1 vol. of Ethyl alcohol and 3 vols. of conc. H_2SO_4 in a flask provided with a dropping funnel and a delivery tube, on a sand bath to a temperature of about 170°C. A few pieces of broken porcelain are added to the mixture to prevent frothing. The gas evolved is first passed through NaOH solution in order to remove CO_2 and SO_2 and then dried by passing through conc. H_2SO_4 and next collected by displacement of mercury.

$$C_2H_5OH + H_2SO_4 = C_2H_4 + H_2SO_4 + H_2O.$$

Sulphuric acid removes the elements of water from ethyl alcohol.

Pure acetylene is obtained by dropping water on lumps of calcium carbide placed in a conical flask provided with a dropping funnel and a delivery tube. Some sand is placed at the bottom of the conical flask on which calcium carbide rests. The water is dropped from the dropping funnel and the gas evolved is passed in succession through $CuSO_4$ solution acidified with H_2SO_4, through a tower containing P_2O_5 and next collected by displacement of mercury.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Methane can be separated from a mixture containing all the three hydrocarbons by first passing the mixture through ammoniacal cuprous chloride solution which absorbs acetylene, giving rise to a red ppt. of cuprous acetylide (Cu_2C_2), then through a wash-bottle containing fuming sulphuric acid, which absorbs ethylene, forming ethyl hydrogen sulphate, $C_2H_5HSO_4$, and then collecting methane by displacement of mercury.

Q. 3. *Describe Precht's process for the manufacture of potassium carbonate. What are the other processes for its preparation ? Is Solvay process applicable for its preparation ? If not, give reasons. What are its uses ? How is potassium detected ?*

Ans. *Precht's process* :—Magnesium carbonate tri-hydrate,

$MgCO_3, 3H_2O$, is taken in the solid state and a concentrated solution of potassium chloride is mixed with it and then carbon dioxide gas (from a lime kiln) is passed into the mixture. A solid is formed, which is a double compound of potassium bicarbonate and magnesium carbonate while magnesium chloride formed passes into solution.

$$3(MgCO_3, 3H_2O)+2KCl+CO_2 \\ =2(MgCO_3, KHCO_3, 4H_2O)+MgCl_2.$$

The solid is separated from magnesium chloride solution by filtration and stirred with water and MgO. The mixture is next heated to 40°C. when potassium carbonate is formed in solution and magnesium carbonate tri-hydrate is re-generated and left as a residue.

$$2(MgCO_3, KHCO_3, 4H_2O)+MgO. \\ =3(MgCO_3, 3H_2O)+K_2CO_3.$$

The solution of potassium carbonate is separated by filtration and evaporated whereby solid K_2CO_3 is obtained.

Potassium carbonate can be prepared from potassium chloride by the application of the principles of Leblanc Process, employed in the manufacture of sodium carbonate from sodium chloride.

(i) $KCl+H_2SO_4=KHSO_4+HCl$

(ii) $KHSO_4+KCl=K_2SO_4+HCl$

(iii) $K_2SO_4+4C=K_2S+4CO$

(iv) $K_2S+CaCO_3=CaS+K_2CO_3$.

Subsequent lixiviation with water, separation from insoluble CaS and crystallisation of the solution by evaporation yields K_2CO_3.

Potassium carbonate can also be obtained by carefully heating cream of tartar (potassium hydrogen tartrate) in covered iron crucibles, the residue being cooled and then extracted with water. The filtered solution is evaporated in silver basins and K_2CO_3 obtained.

Potassium carbonate cannot be manufactured by Solvay process, because potassium bicarbonate formed in the operation is very soluble in water and so does not separate out in the solid state like $NaHCO_3$.

Uses :—Potassium carbonate is largely employed in the manufacture of soft soap, potassium ferrocyanide, potassium chromate, potassium bromide and potassium iodide. It is also used in the manufacture of hard glass. In the laboratory it is used, admixed with sodium carbonate, in fusion mixture.

Potassium in potassium compounds can be detected by taking a small amount of the compound of potassium on a Platinum wire, moistening it with conc. HCl and then holding the wire with the moistened compound in a non-luminous Bunsen flame, when the flame is coloured pale violet. The colour of the flame appears red when it is viewed through double blue glass.

In the wet way, potassium can be detected in potassium compounds by adding a solution of chloroplatinic acid to their aqueous solution when a yellow ppt. of potassium chloroplatinate (K_2PtCl_6) is formed.

Q. 4. *You are supplied with the following substances in different test tubes—(a) ammonium nitrate, (b) magnesium carbonate, (c) Copper sulphate, (d) ferrous chloride. Can you identify them from appearance and colour ? How would you detect chemically the various radicals present in the substances supplied ?*

Ans. Ammonium nitrate and magnesium carbonate are both white solids, but the former one in crystalline and the second one is non-crystalline powder. So close observation may help in identifying the two materials present in two of the test tubes. Copper sulphate and ferrous chloride are recognised by their colour, the former being blue in colour and the latter light green.

(*a*) When a little of the crystalline solid is rubbed with soda lime in a mortar, the smell of ammonia is perceived. Further confirmation can be obtained by taking a very small amount of the material in another test tube in aqueous solution and adding Nessler's solution to it, when a brown ppt. is produced.

The presence of the nitrate radical is shown by adding ferrous sulphate solution to a little quantity of it taken in a test tube, then holding the test tube in a slanting position under running water from a tap and next adding conc. H_2SO_4 to the mixture. The appearance of a brown ring at the junction of conc. H_2SO_4 (bottom layer) and ferrous sulphate solution (top layer) confirms the presence of nitrate radical. উত্তরপাড়া জয়কৃষ্ণ

$$6FeSO_4 + 2NH_4NO_3 + 4H_2SO_4$$
$$= 3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 2NO + 4H_2O$$
$$FeSO_4 + NO = FeSO_4, NO \text{ (brown ring).}$$

(*b*) When magnesium carbonate is heated on charcoal under the oxidising blowpipe flame, a white incandescent residue of MgO is left behind. This white residue, on being moistened with a drop of cobalt nitrate solution and heated again in the oxidising blowpipe flame becomes *pink* in colour.

The confirmation in the wet way can be carried out by dissolving a little of the white powder in dil. HCl, then adding ammonium chloride, ammonia in excess and ammonium carbonate to the solution when no ppt. appears. Next disodium hydrogen phosphate solution is added and the test tube is vigorously shaken and the sides of the reaction vessel is scratched with a glass rod when a white crystalline precipitate of magnesium ammonium phosphate is obtained.

Carbonate is detected by adding dilute H_2SO_4 to a little of the powder taken in a test tube fitted with a cork to which a bent delivery tube is attached. Effervesence occurs and the gas evolved, when passed into lime-water contained in another test tube, turns lime-water milky.

(*c*) Copper is detected in the blue substance by dissolving a little of the material taken in a test tube in water and then gradually adding ammonia to it. At first a bluish white precipitate is formed, which dissolves on adding excess of ammonia forming a deep blue solution. On acidifying the solution with acetic acid and adding potassium ferrocyanide solution, a chocolate precipitate of copper ferrocyanide appears, confirming the presence of copper.

To the aqueous solution of the substance, barium chloride solution is added. The appearance of a precipitate, insoluble in all mineral acids, indicates the presence of sulphate radical. The precipitate will be seen to be white on filtering and washing thoroughly with hot water when the adhering copper salt is completely removed.

(*d*) To an aqueous solution of the salt, potassium ferricyanide solution is added when a deep blue precipitate is formed. To confirm further the presence of iron, a little of the substance is taken and boiled with nitric acid in a test tube. Then an excess of ammonia is added to it, when a brown precipitate of ferric hydroxide is formed. The precipitate is dissolved in dil. HCl and potassium ferrocyanide is added to it, when a deep-blue precipitate is formed. This confirms the presence of iron in the substance.

Chloride is confirmed by adding silver nitrate solution to an aqueous solution of the sample, when a curdy white precipitate is formed, which is insoluble in HNO_3 but soluble easily in dilute ammonia.

Q. 5. *Explain the following statements with illustrations :—*

(*a*) *Matter is indestructible,*

(*b*) *Combustible and supporter of combustion are reciprocal terms.*

(*c*) *The process of oxidation and reduction are complementary.*

Ans. (*a*) Law of conservation of matter states : "Matter can neither be created nor destroyed, but can be transformed from one form into the other." This is verified by the following experiment.

A flask is taken fitted with a tightly fitting rubber cork. Through the cork two thick copper wires carrying a copper spoon at the end are fitted. A bit of charcoal is placed on the copper spoon. The two thick copper wires near the spoon are wound round with a thin platinum wire so that the two copper wires are in contact through the Pt-wire and the platinum wire is made to touch the bit of charcoal. The rubber cork with the copper wires carrying the spoon is removed, and the air inside the flask is replaced by oxygen. The cork with the wires carrying the spoon in which the bit of charcoal is placed is then replaced in its original position so that it tightly closes the mouth of the flask. Then the flask with its contents is weighed in a chemical balance. The copper wires projecting outside the cork are then connected to the terminals of a battery, and a current is passed. The Pt-wire becomes red-hot due to resistance offered by this wire and this ignites the bit of charcoal in contact with it and the bit of charcoal burns readily in the oxygen gas. After the flame is extinguished, the

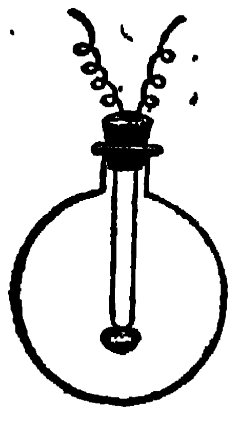


Fig. 139

wires connecting the battery are disconnected, the apparatus cooled and weighed in a chemical balance. The weight is found to be the same as before. Thus, although most of the charcoal has disappeared by burning, yet no loss in weight is recorded. Hence nothing is lost by burning away of the bit of charcoal.

The best experiments for establishing the truth of the statement that "matter is indestructible" are those carried out by Landolt for 15 years till 1908.

In one of his experiments Landolt took solutions of ferrous sulphate and silver sulphate in two different arms of a H-shaped tube as shown in the adjoining figure. These two substances were chosen because they would react together without the production of *much* heat. The ends of the H-tube were next sealed in order that there might not be any mechanical loss of materials. The tube was next weighed accurately in a sensitive balance using another such H-tube as a counterpoise. Then the two solutions were carefully mixed together by tilting the tube. A chemical reaction occurred and metallic silver was deposited due to the reducing action of ferrous sulphate.

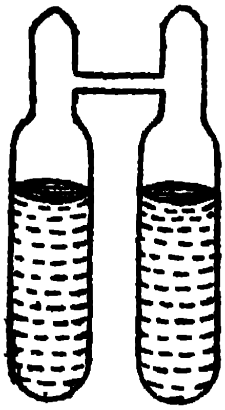


Fig. 140

$$Ag_2SO_4 + 2FeSO_4 = Fe_2(SO_4)_3 + 2Ag.$$

After the reaction was over, the tube was allowed to cool for some time and then weighed in the same balance by using the same counterpoise. Landolt found that the weight remained practically constant, though there was an apparent creation of matter.

It is clearly seen from the two experiments described that there has been no destruction of matter.

N. B. Since only indestructibility of matter is to be proved the first experiment is sufficient to establish it.

(*b*) Any chemical reaction accompanied by the evolution of heat and light is called *combustion*. Now it is customary to classify the substances taking part in combustion as the combustible bodies and supporters of combustion. Usually we call those substances which burn *combustible* and the atmosphere surrounding the burning substances, *supporter of combustion*.

Thus paraffin, hydrogen, carbon monoxide, etc. are combustible substances ; while oxygen, air, etc. are supporters of combustion.

This distinction, however, is a purely conventional one, and the two terms are purely relative. By a slight modification of the conditions, either H_2 or CH_4 or coal gas may become supporters of combustion and O_2 or Cl_2 the combustible bodies. This can be illustrated by the following experiment :—

A glass chimney is taken provided with a cork at its bottom. Two glass tubes, one short and the other long, is inserted through the cork at the bottom. A small sheet of asbestos with a hole at the middle is placed at the top of the chimney. Hydrogen is passed through the short tube till the chimney is completely filled up with hydrogen. Hydrogen is ignited as it comes out at the top through the hole in the asbestos. Now oxygen is passed in through the long tube and the gas is ignited by pushing the long tube up to the burning hydrogen. The long tube is then drawn into the middle of the chimney. We have got here two flames ; one at the top of the chimney. where hydrogen burns in oxygen of air, and the other inside the chimney where oxygen burns in hydrogen. Similar experiment can be performed with coal gas and oxygen or chlorine and hydrogen. Thus the supporter of combustion in one case can be made combustible in the other. Hence the terms are reciprocal.

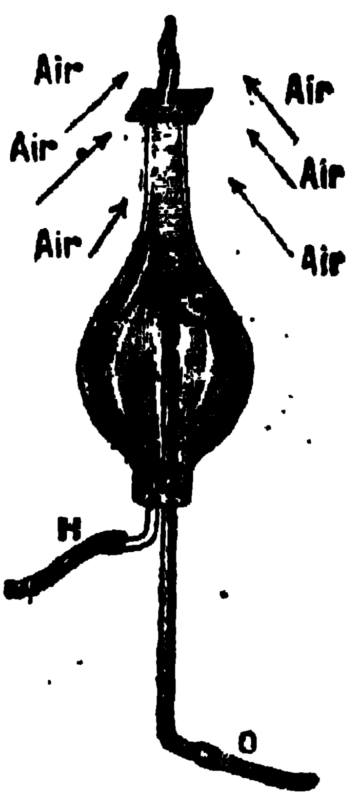


Fig. 141

(c) The expression means that whenever a substance undergoes oxidation, it does so at the expense of some other substance which undergoes reduction at the time when the first one is oxidised. Thus, in the reaction between stannous chloride and mercuric chloride, stannous chloride is oxidised to stannic chloride, while at the same time mercuric chloride is reduced to mercurous chloride.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

Similarly in the reaction between sulphuretted hydrogen and sulphur dioxide, sulphuretted hydrogen is oxidised to sulphur at the expense of sulphur dioxide which is simultaneously reduced to sulphur.

$$2H_2S + SO_2 = 2H_2O + 3S.$$

Thus oxidation and reduction always go hand in hand.

Q. 6. *Give the names and compositions of the chief ores of copper and explain the chemistry of the extraction of the metal from its sulphide ores. Mention the uses of the metal and its alloys. Is copper are available in India ?*

Ans. Chief Ores of Copper

Ruby ore—Cu_2O
Copper glance—Cu_2S
Copper pyrites—Cu_2S, Fe_2S_3 or $Cu Fe S_2$
Purple copper Ore — $3Cu_2S, Fe_2S_3$ or $Cu_3Fe S_3$
Malachite, $CuCO_3, Cu(OH)_2$
Azurite, $2CuCO_3, Cu (OH)_2$

Extraction of copper from sulphide ores, viz., copper pyrites—Copper is extracted by a Thermal process by the following operations :—

At first the ore is concentrated either by gravity separation or by floatation process. For this purpose the ore is first crushed and finely powdered. The powdered ore is next churned with water containing a little oil and lime, by blowing air through it. By this operation a froth is produced, which carries up along with it the particles of Cu-ore, leaving sand and other impurities behind. The froth is collected by skimming and allowed to settle.

The concentrated ore is next roasted in multiple hearth furnace, whereby excess of sulphur present is burnt out to SO_2 and the metals viz. Fe present in pyrites and Cu. are partially oxidised.

$$Cu_2S,Fe_2S_3 + O_2 = Cu_2S + 2FeS + SO_2$$
$$Cu_2S,Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$
$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$

this last reaction occurring only to a very small extent. The roasted ore is next mixed with coke, sand (or slag from subsequent operations) and a little quantity of lime and the mixture heated in a water-jacketed blast furnace when a little quantity of Cu_2O formed in the previous operation reacts with iron sulphide giving Cu_2S and FeO.

$$Cu_2O + FeS = Cu_2S + FeO.$$

The ferrous oxide so formed and also produced in the previous operation reacts with sand or silica, giving a slag of ferrous silicate, $FeO + SiO_2 = FeSiO_3$. The slag is removed and the residue obtained of cuprous and ferrous sulphide is known as *matte.* The molten matte is then directly run into a Bessemer converter with a little silica and a blast of air is introduced through tuyeres placed at the sides. Iron is first oxidised to FeO which combines with silica forming a slag of ferrous silicate as before. The slag is removed and the blast continued. Cu_2S is then partially oxidised to Cu_2O and this Cu_2O reacts with unchanged Cu_2S to form Copper and SO_2. The slag is removed, the blast stopped and the converter tilted to pour off Cu. This copper has a blistered appearance due to escape of SO_2.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$

Blistered copper is then melted on the hearth of a reverberatory furnace when the impurities are oxidised. Some escape as gas, others form slag with the furnace lining of silica, which is removed. Next the metal begins to oxidise. Anthracite coal in the form of powder is then sprinkled on the molten mass and the mass is stirred with logs of green wood. When the copper attains the requisite *tough-pitch,* it is poured out.

Further purification of copper can be effected by electrolysis. Thick sheets of impure copper are suspended from a metal rod in a bath of $CuSO_4$ solution, acidified with 15% sulphuric acid, and taken in an wooden vessel lined with lead. Thin plates of pure copper are suspended from another metal rod and are dipped in the same bath in such a fashion that these are inserted alternately between the thick sheets. The rod carrying the thin sheets of pure copper is connected to the negative pole of a battery and thereby the thin sheets of pure copper are made to function as cathodes. Also the rod carrying the thick slabs is connected to the positive pole of the same battery, thus making the thick slabs to function as anodes. On passing electric current through the bath of copper sulphate, copper ions pass into solution from thick sheets gradually and are deposited as pure metallic copper on thin sheets after neutralisation of charge on them. Impurities present either pass into solution or are deposited at the bottom of the bath near the anodes as *anode slimes.* Copper, thus obtained as a deposit on the cathode, is 99·99% pure.

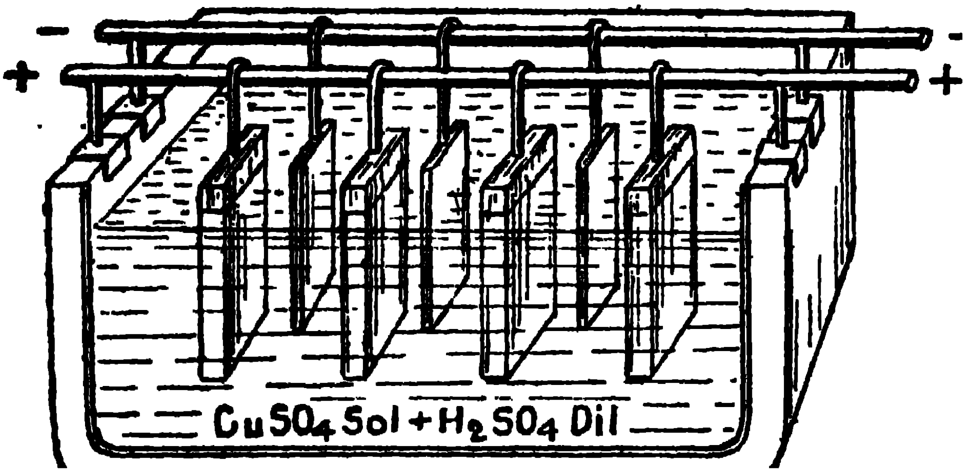


Fig. 142

Uses of copper and its alloys :—

Copper is largely used in electric industry, in electro-typing, for cables and wires for conveying electric current, and in setting up voltaic cells ; it is also used in the preparation of household utensils, for coinage and for the preparation of alloys, like brass, bronze, German silver, etc.

Brass is one important alloy of copper and zinc. It is used for preparing house-hold utensils, cartridge cases and in machinery parts. *Bronze* is another alloy of copper with tin. It is used for making medals, statues, etc. Alloyed with a little amount of zinc, bronze is used in coinage. *German silver* is an alloy of copper, zinc and nickel. It is used for the preparation of cheap ornaments as also utensils for every-day use.

Yes, copper ores are available in India ; they are found in the Singbhum District of Bihar, Nellore, Sikkim and Bhutan.

Q. 7. *Starting from metallic lead, how would you prepare—litharge, red lead, and lead dioxide ? By what tests would you distinguish between these oxides ? How is lead detected ?*

Ans. *Litharge* is crystalline lead monoxide. It is prepared from metallic lead by heating the latter in contact with air, when massicot is first formed ; when this massicot is melted by the application of sufficient heat and the molten massicot is cooled crystalline litharge is formed.

$$2Pb + O_2 = 2PbO.$$

Red lead is obtained from metallic lead in the following way. First metallic lead is heated in a current of air, when it is converted into PbO. This PbO is removed from the furnace and hammered, when any particles of unoxidised lead is flattened out. Powdery PbO is then removed by sieving. Finely powdered PbO is then heated in a barrel-shaped vessel, open at both ends, in excess of air at 400°C. for 48 hours, whereby red lead is formed. It is removed, washed and dried.

$$6Pb + 3O_2 = 6PbO$$
$$6PbO + O_2 = 2Pb_3O_4.$$

For preparation of lead dioxide from metallic lead, first of all red lead is prepared from metallic lead and then the red lead so obtained is treated with conc. HNO_3 in the cold. The solution so obtained is diluted with water, and the diluted solution is filtered. The residue is lead dioxide, PbO_2. It is washed and dried.

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

The following are the tests by which the three oxides can be distinguished :—

(1) Colour of the three oxides are different. So by observing the colour the three oxides can be differentiated. Litharge is yellow, red lead is deep red in colour, whereas lead peroxide is chocolate-brown in colour. Moreover, litharge and red lead are crystalline, whereas lead dioxide is amorphous in character.

(2) Conc. HNO_3 is one reagent by means of which we can distinguish between these oxides.

Litharge will dissolve in the acid without leaving any residue. Red lead will be converted into chocolate-brown amorphous powder by treatment with cold conc. HNO_3. The solution, on filtration, will respond to the tests for lead nitrate. Cold conc. HNO_3 has no action on lead dioxide.

(3) Conc. HCl is another reagent by means of which litharge can be differentiated from red lead and lead dioxide.

On heating to boiling with conc. HCl, litharge will dissolve completely without evolution of any gas. On cooling, white glistening crystals of $PbCl_2$ will be deposited.

$$PbO + 2HCl = PbCl_2 + H_2O.$$

On heating red lead and lead peroxide with conc. HCl to boiling, chorine gas, yellowish-green in colour and possessing the smell of bleaching powder, is evolved. The solution, on cooling, deposits $PbCl_2$.

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O$$
$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

Lead can be detected in the dry way by heating any compound of lead mixed with Na_2CO_3 on a charcoal block under the reducing blowpipe flame, when a soft metallic bead of lead with a *lemon-yellow* incrustation on charcoal block is obtained. The bead can be flattened by harmmering and it marks paper. In the wet way, on adding dil. HCl to a lead-salt solution, a white precipitate of $PbCl_2$ is produced in the cold. On boiling the solution the precipitate dissolves, but reappears on cooling as white glistening needle-shaped crystals.

Also on adding KI solution to a solution of a lead salt, yellow precipitate of PbI_2 is produced. On heating the precipitate with water to boiling, it dessolves, but on cooling *golden spangles* of PbI_2 separate out.

Q. 8. *Explain, giving equations, what happens when :—*

(*a*) *Zinc is added to a solution of copper sulphate,*

(*b*) *A mixture of alumina and coke is heated in chlorine,*

(*c*) *Stannous chloride solution is added gradually to a solution of mercuric chloride,*

(*d*) *Each form of phosphorous is boiled with caustic soda solution.*

Ans. (*a*) Zinc displaces copper from copper sulphate solution, as zinc occurs above copper in the electro-chemical series. Zinc sulphate passes into solution.

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

(*b*) In presence of chlorine coke helps in reducing alumina to metallic aluminium which immediately combines with chlorine forming anhydrous aluminium chloride. This $AlCl_3$ formed is volatile at the temperature of the reaction and so can be collected in a cooled dry receiver as a solid by sublimation.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

(*c*) At first stannous chloride added in small amount reduces mercuric chloride to mercurous chloride which is obtained as a silky-white precipitate. On adding further quantity of stannous chloride solution, mercurous chloride is reduced to gray metallic mercury.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$
$$SnCl_2 + Hg_2Cl_2 = 2Hg + SnCl_4.$$

Stannous chloride is oxidised to stannic chloride in the reaction, which remains in solution.

(*d*) Red phosphorus does not react with boiling caustic soda solution. But white phosphorus reacts with boiling caustic soda solution with the evolution of phosphine and formation of sodium hypophosphite in aqueous solution.

$$4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2.$$

FIRST PAPER—1958

Q. 1. *What are the important constituents of air ?*

Describe how you would prove that air is a mixture and not a compound.

Ans. The important constituents of air are : (*i*) Oxygen, (*ii*) Nitrogen, (*iii*) Carbon dioxide and (*iv*) Water vapour, Besides, air contains inert gases like Argon, Helium, Neon, Krypton and Xenon.

The following are the reasons for considering air to be a mechanical mixture of nitrogen and oxygen :—

(1) In a mechanical mixture of two or more substances the properties of the different ingredients are retained, but when a compound is formed from two or more ingredients, the molecules of the ingredients are changed and new molecules are formed. These new molecules have properties altogether different from those of the ingredients.

Thus, the properties of both nitrogen and oxygen are found to be present in air ; for example, oxygen is a supporter of combustion, so is also air, though to a less extent on account of its dilution. Oxygen is absorbed by the alkaline pyrogallate. But alkaline pyrogallate cannot remove oxygen by absorption from any of the oxides of nitrogen which are compounds of nitrogen and oxygen. After removal of oxygen from air by absorption with alkaline pyrogallate, nitrogen left shows all the properties of nitrogen.

Therefore air is considered to be a mechanical mixture.

(2) The analyses of samples of air drawn from different localities and different altitudes show that the proportion of nitrogen and oxygen in air by weight is *nearly* constant, yet slight variations are noticeable. But even the slightest deviation is not possible in the case of a chemical compound.

Air is thus a mixture of oxygen and nitrogen.

(3) When gases combine chemically there is always a thermal effect, and oftentimes a change in volume is observed. But when 23 parts by weight of oxygen are mixed with 77 parts by weight of nitrogen, there is neither any heat change nor any change in volume. Yet the mixture behaves in every way like ordinary air.

Thus, air is a mechanical mixture.

(4) The density and other physical properties of air are average of these properties of the constituents, nitrogen and oxygen, in the proportion in which they are present in air. Thus, taking d to be the density of air which contains nitrogen and oxygen in the proportion 4 : 1 by volume approximately, we can calculate d as follows :—

Wt. of air = Wt. of nitrogen + wt. of oxygen. Taking into consideration 100 vols. of air to be formed from 80 volumes of nitrogen and 20 vols. of oxygen,

$$\begin{aligned} 100 \times d &= 80 \times 14 + 20 \times 16 \\ &= 1120 + 320 \\ &= 1440 \\ \therefore \quad d &= 14{\cdot}4 \end{aligned}$$

The observed density of air is also 14·4—just the value calculated on the assumption that air is a mechanical mixture.

Therefore air is nothing but a mechanical mixture.

(5) There are five different oxides of nitrogen whose gravimetric compositions are such that they obey the *Law of Multiple proportions.* The composition of air by weight (77 nitrogen : 23 oxygen) is such that no simple formula can be assigned to it. (77 parts by weight of nitrogen stand for 5½ atoms of nitrogen and 20 parts by weight of oxygen stands for 1·4075 atoms of oxygen). Thus the Law of Multiple proportions as applicable to the case of definite oxides of nitrogen cannot be applied here.

Therefore air is a mechanical mixture.

(6) The ingredients of a mechanical mixture can be separated by easy mechanical means of separation like diffusion, distillation, vaporisation, etc., but the components of a chemical compound cannot be so separated.

The constituents of air can be separated

(*a*) *By diffusion* : When air is passed through a porous tube, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen and the residue left is found to be richer in oxygen than ordinary air. Had air been a chemical compound, no such separation of the constituents would have been possible.

(*b*) *By vaporisation* : When liquid air is allowed to evaporate, the boiling point increases progressively. Further, the gas which comes out first is richer in nitrogen than the gas which comes out afterwards. Thus, liquid air is to be considered as a mixture of two liquids, liquid nitrogen and liquid oxygen, and it may be presumed that atmospheric air is also a mixture of the gases, nitrogen and oxygen.

(*c*) *By solution in water* : If air be shaken with water a part of it goes into solution and the dissolved gas can be expelled by boiling. It has been found that the air thus recovered from solution is very much richer in oxygen than ordinary air. Thus a partial separation of the ingredients of air by solution in water followed by subsequent heating, *i.e.*, by easy mechanical means is possible.

Air is thus a mechanical mixture.

Any single argument given in the above discussion may not be considered sufficient, but the arguments taken all together prove completely that air is a mechanical mixture, and *not a compound*, of nitrogen and oxygen.

Q. 2. (*a*) *Discuss the effects of pressure and temperature on the volume of a given mass of a gas.*

(*b*) *A given mass of a gas occupies a volume of 2·5 litres at 0°C and 76cm. pressure of mercury. Find its volume at 546°C and 150cm. pressure of mercury.*

Ans. (*a*) The volume of a given mass of a gas changes with change of pressure as also with change of temperature. All gases obey two laws, one relating to effect of change of pressure, known as Boyle's Law, and the other relating to the effect of change of temperature, known as Charles' Law. Boyle's Law states that *temperature remaining constant, the volume of a given mass of any gas is inversely proportional to its pressure.*"

Charles' Law states that "pressure remaining constant, the volume of a given mass of any gas increases by $\frac{1}{273}$ part of its volume at 0°C for each degree rise of temperature."

So with increase of pressure, the volume of a given mass of a gas diminishes and with increase of temperature the volume increases.

From Charles' Law, it can be deduced that the volume of a given mass of any gas is directly proportional to its absolute temperature, pressure remaining constant.

(*b*) From Boyles' Law and Charles' Law it has been deduced that

$\frac{P \times V}{T} = \frac{P_1 \times V_1}{T_1}$, where P, V and T are pressure, volume and absolute temperature of a given mass of any gas and P_1, V_1 and T_1 are another set of values of pressure, volume and absolute temperature of the same mass of gas.

Here,

$P = 76$ cm. $\quad$ $P_1 = 150$ cm.

$V = 2·5$ litres. $\quad$ $V_1 = ?$

$V = (273 + 0)^\circ$ Abs. $\quad$ $T_1 = (273 + 546)^\circ$ Abs

$= 273^\circ$ Abs. $\quad$ $= 819^\circ$ Abs.

Then, we have

$$\frac{76 \times 2{\cdot}5}{273} = \frac{150 \times V_1}{819}$$

$$V_1 = \frac{76 \times 2{\cdot}5 \times 819}{273 \times 150} \text{ litres}$$

$$= 3{\cdot}8 \text{ litres.}$$

Q. 3. *Describe how you would prepare concentrated nitric acid. State what happens when it is allowed to act on (a) tin, (b) iodine and (c) sulphur; the acid is hot in the cases of (b) and (c).*

Ans. Equal parts by weight of Potassium nitrate and conc. Sulphuric acid are taken in a stoppered retort, the stem of which is introduced into a small flask floating on and kept cooled by water as shown in the adjoining figure. The mixture is heated gently, when Potassium nitrate reacts with sulphuric acid producing Nitric acid which distils over and collects inside the small flask. The residue left in the retort consists mainly of Potassium hydrogen sulphate.

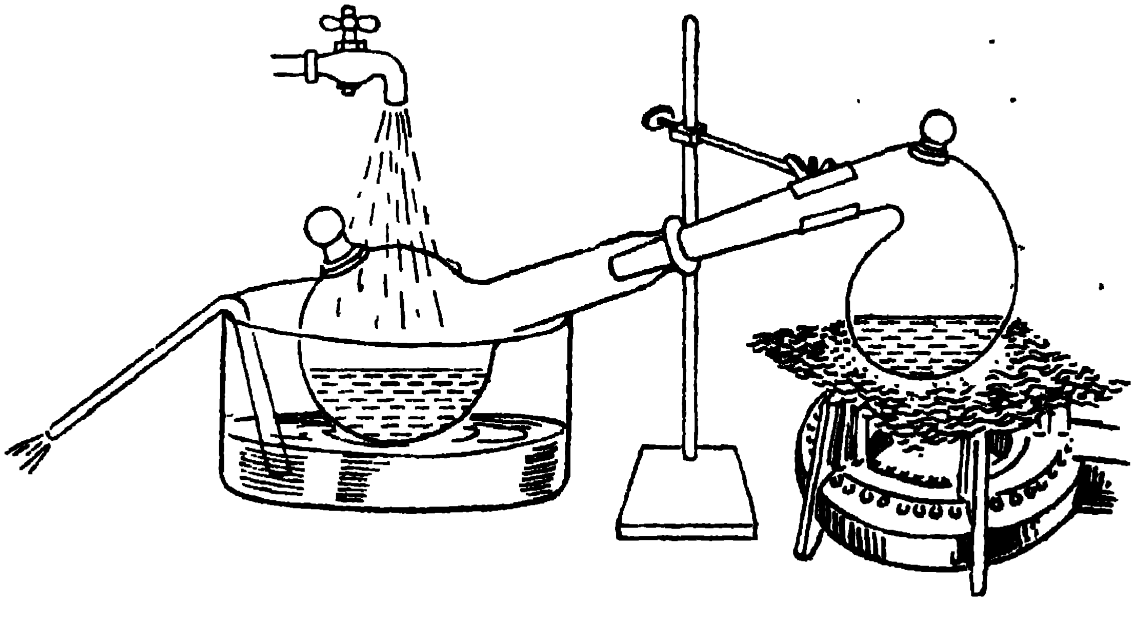


Fig. 143

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

The acid thus obtained is some-what dilute and impure. The concentration and purification of the acid is carried out by mixing the acid collected in the small flask with concentrated Sulphuric acid and then distilling the mixture fractionally. The first ⅓rd portion of the distillate is rejected. The second ⅓rd portion is collected and while slightly warm, a steam of dry air or CO_2 is blown through it, till the liquid becomes colourless. The acid now contains 99·8% of the anhydrous acid and is pure.

Residue left in the retort (last ⅓rd portion) is rejected.

(*a*). Pure and highly concentrated Nitric acid (sp-gr. 1·4) has no action on tin. But on adding a drop of water after adding the conc-HNO_3 to metallic tin, violent action takes place and voluminous powder of metastannic acid is produced.

$$5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 20NO_2 + 5H_2O$$

(*b*) Hot and concentrated Nitric acid oxidises iodine to iodic acid, HIO_3.

(*i*) $I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$.

(*ii*) $3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$.

Oxides of nitrogen are evolved as gas.

(*c*) Hot and concentrated Nitric acid oxidises sulphur to sulphuric acid and nitric oxide is evolved as gas.

$$S + 2HNO_3 = H_2SO_4 + 2NO.$$

Q. 4. *What are the sources of Bromine? How is it manufactured? Describe its action on (a) a solution of Sodium sulphite and (b) a cold dilute solution of Caustic soda. Give equation in each case.*

Ans. Sources of bromine are: (1) Stassfurt Carnallite, $KCl, MgCl_2, 6H_2O$, which contains $MgBr_2$ as impurity in the form of bromocarnallite, $KBr, MgBr_2, 6H_2O$ in very small amount; (2) Sea-water, which contains very small amount of bromides of sodium and magnesium.

Manufacture of Bromine :—

(1) Bromine is manufactured in America (Dow Chemical Works) from sea-water. Sea-water is drawn at a point near the Works, and collected in a tank. It is then acidified and next chlorinated. Bromine liberated from bromides colours the sea-water to light straw-yellow. The dissolved bromine is blown out by a current of air and is absorbed in Na_2CO_3 solution. Sodium bromide and sodium bromate are formed in solution. The solution is next treated with excess of sulphuric acid and bromine set free is distilled off in steam.

$$3Na_2CO_3 + 3Br_2 = 5NaBr + NaBrO_3 + 3CO_2$$

$$NaBrO_3 + 5NaBr + 3H_2SO_4 = 3Br_2 + 3Na_2SO_4 + 3H_2O.$$

Water is removed by distilling the product with conc. H_2SO_4.

(*ii*) At Stassfurt, in Germany, Bromine is manufactured from carnallite, which is first dissolved in water and the solution concentrated, whereby KCl crystallises out and is removed. The *mother-liquor* (known as *bittern*) contains magnesium chloride together with magnesium bromide. The hot mother-liquor (at about 60°C) is allowed to slowly trickle down a tower packed with earthenware balls; the tower is connected with a tank situated below, which is provided with zig-zag shelves. The mother liquor circulates round the zig-zag shelves inside the tank. Steam is blown into the tank and a stream of chlorine gas is introduced by a pipe situated above the tank and fitted to the bottom of the tower, as shown in the adjoining figure. Chlorine sets free Bromine from magnesium bromide.

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$

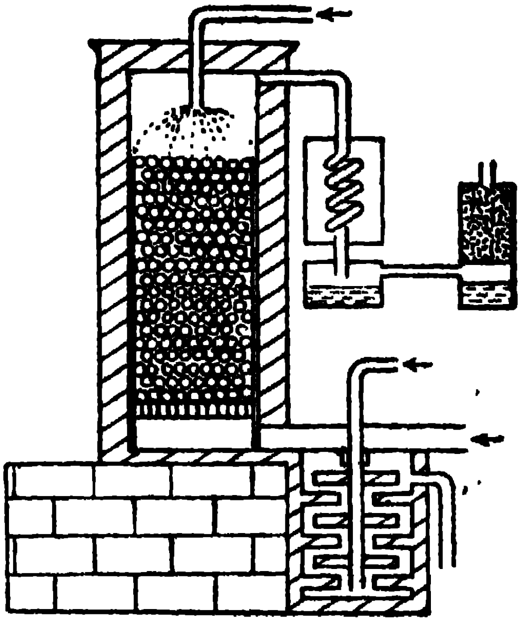


Fig. 144

Bromine, thus liberated, both in the tower and in the tank, is converted into vapour by steam. Bromine-vapour travels up and escapes by means of an outlet at the top. It is condensed by passing through spiral condenser. Any uncondensed bromine-vapour as also chlorine are absorbed in *moist* iron-filings.

Bromine thus obtained, is not pure. It contains chlorine, iodine and water as impurities. It is purified by first distilling with KBr solution (for removal of chlorine), then with ZnO (for removal of iodine). The second distillate is mixed with conc. H_2SO_4 and distilled (for removal of water).

(a) Bromine oxidises Sodium sulphite solution to Sodium sulphate solution, and itself reduced to Hydrobromic acid.

$$Na_2SO_3 + Br_2 + H_2O = Na_2SO_4 + 2HBr.$$

(b) Bromine reacts with a cold dilute solution of caustic soda with the production of Sodium bromide and Sodium hypobromite in solution. Water is also formed.

$$Br_2 + 2NaOH = NaBr + NaOBr + H_2O.$$

Q. 5. *Describe what happens when (a) Chlorine, (b) Sulphur dioxide and (c) red phosphorus are allowed to act separately on iodine suspension in water. Give equation in each case.*

Ans. (a) When chlorine is continuously passed into iodine suspension in water, gradually iodine is used up with the production of iodic acid which remains in solution. Hydrochloric acid is also formed in solution. Gradually a colourless solution is obtained. Here chlorine oxidises iodine to iodic acid, itself being reduced to hydrochloric acid.

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

(*b*) Iodine suspension in water reacts with sulphur dioxide with the production of hydriodic acid and sulphuric acid in solution. Here iodine oxidises sulphur dioxide to sulphuric acid and is itself reduced to hydriodic acid.

$$I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI.$$

(*c*) At first red phosphorus and iodine react with the production of phosphorus tri-iodide, PI_3 and this PI_3 is subsequently decomposed by water present with the production of phosphorous acid, H_3PO_3 and hydriodic acid, HI.

$$2P + 3I_2 = 2PI_3$$

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

Q. 6. *Explain and illustrate the following :—*

(*a*) *Water of crystallisation,* (*b*) *Catalyst,* (*c*) *Oxidation and reduction.*

Ans. (*a*) Many solid substances, when crystallising out of their aqueous solutions, give rise to crystals containing combined water, taken up from the solution. Each molecule of the crystalline solid is found to contain a definite number of molecules of water. The particular crystalline shape and sometimes the colour of the crystalline solid depend upon these combined molecules of water. When the water is removed from the crystalline solid, it loses its particular crystalline shape and the colour in case of coloured crystals. Water so associated with crystals as an essential part of their constitution is known as *water of crystallisation.*

For example, copper sulphate pentahydrate (blue crystals), $CuSO_4$, $5H_2O$, may be mentioned. When heated above 250°C, it loses all the 5 molecules of water associated with 1 molecule of $CuSO_4$ and then it becomes colourless and powdery, the crystalline shape being destroyed.

Ferrous sulphate heptahydrate (Green crystals), $FeSO_4$, $7H_2O$ is another example in point. Here 1 molecule of $FeSO_4$ is associated with 7 molecules of water of crystallisation.

(*b*) A catalyst is a substance which, when present in a comparatively small amount, either increases or diminishes the rate of a chemical reaction without itself undergoing any change in mass and in chemical composition at the end of the reaction.

When the substance helps in increasing the rate of a chemical reaction, it is called a *positive catalyst.* For example, manganese dioxide in small amount added to potassium chlorate helps to accelerate the rate of decomposition by heat of $KClO_3$ with the evolution of oxygen and so MnO_2 acts there as a positive catalyst.

But when the substance helps in retarding or diminishing the velocity of a chemical reaction, it is called a *negative catalyst.* For example, phosphoric acid, when added in small amount to a solution of hydrogen peroxide, retards the rate of spontaneous decomposition of hydrogen peroxide and so H_3PO_4 acts there as a negative catalyst.

(*c*) **Oxidation** is described as the process which increases the proportion of oxygen or of an equivalent electro-nagative element or radical in an element or a compound, or diminishes the proportion of hydrogen or of an electro-positive element or radical in a compound,

Reduction may be defined as the result of the converse operations. Thus, **reduction** is the process which increases the proportion of hydrogen or of an electro-positive element or radical in an element or a compound or diminishes the proportion of oxygen or of an equivalent electro-negative element or radical in a compound.

Thus, when sulphur is burnt in oxygen, it is **oxidised** to sulphur dioxide.

$$S + O_2 = SO_2.$$

When iron is heated in a stream of chlorine gas, it is oxidised to ferric chloride.

$$2Fe + 3Cl_2 = Fe_2Cl_6.$$

When hydrochloric acid is heated with manganese dioxide, it is oxidised to chlorine by removal of hydrogen.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

Similarly when hydrogen gas is passed over heated copper oxide (black), it is reduced to metallic copper (red).

$$CuO + H_2 = Cu + H_2O.$$

When sulphuretted hydrogen is passed into iodine suspended in water, iodine is reduced to hydriodic acid by addition of hydrogen.

$$H_2S + I_2 = 2HI + S.$$

When ferric chloride solution (yellow) is treated with zinc and hydrochloric acid, it is reduced to ferrous chloride (solution colourless) by nascent hydrogen.

$$FeCl_3 + H = FeCl_2 + HCl.$$

Among inorganic compounds, oxidation usually denotes an increase in the active valency of the central atom, as for example, when ferrous chloride is oxidised to ferric chloride, or stannous chloride is oxidised to stannic chloride.

From ionic standpoint, if we take into consideration the reaction,

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2$$

it can be represented as

$$2Fe^{+++} + Sn^{++} = Sn^{++++} + 2Fe^{++}.$$

Here it is evident that stannous ion is oxidised by the loss of two electrons which have passed to the ferric ions, reducing them to the ferrous state.

Hence, *oxidation* may be defined as *a loss of electrons* and *reduction* as *a gain of electrons.*

Moreover, it must also be observed that oxidation and reduction take place simultaneously. Whenever a substance is oxidied, another one is reduced. Thus, when stannous chloride solution is added to a solution of mercuric chloride, a white precipitate of mercurous chloride is obtained. Here mercuric chloride is reduced to mercurous chloride, but at the same time stannous chloride is oxidised to stannic chloride.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

Q. 7. *You are given a finely powdered mixture of sodium chloride, carbon and sulphur. Describe how you would separate them from one another.*

Ans. The powdered mixture is taken in a basin, carbon disulphide is added to the mixture and the mixture thoroughly stirred with a glass rod. The insoluble portion is allowed to settle and the liquid carbon disulphide containing dissolved sulphur is poured through a filter paper fitted to a funnel. The filtrate is collected in an evaporating dish. The residue is again treated with a further quantity of carbon disulphide with thorough stirring to dissolve out all the sulphur present in the mixture. The mixture is then filtered again, and the filtrate is caught in the same evaporating dish as before. On exposing the evaporating dish to air, carbon disulphide evaporates away, leaving sulphur behind.

The residue on the filter-paper, on exposure to air, loses all carbon disulphide adhering to the residue. Then it is taken in a beaker, sufficient water is added to it and boiled. Sodium chloride dissolves in the boiling water. The mixture is filtered hot, the filtrate being collected in an evaporating dish. The residue is again taken in the beaker and boiled with water to dissolve out all the sodium chloride. The mixture is again filtered hot and the filtrate collected in the same evaporating dish as before. The evaporating dish is next placed on a boiling water-bath and water evaporated away. Thus solid sodium chloride is recovered.

The residue on the filter-paper is washed thoroughly with hot water and dried, when charcoal is obtained free from sodium chloride.

Q. 8. *Describe how you would prepare pure and dry ammonia. Narrate its three important physical and three important chemical properties. Describe one method of determining its volumetric composition.*

Ans. Preparation of *pure* and *dry* ammonia in the *laboratory* is carried out by heating *dry* powdered ammonium chloride with about twice its weight of powdered quicklime in a hard glass test tube closed by a cork through which a delivery tube is fitted. The hard glass test-tube is clamped in a slightly inclined position to a retort stand and the delivery tube is joined to the bottom of a lime-tower, filled with quicklime, as shown in the figure, An upright delivery tube is next fitted to the top of the lime-tower as shown in the figure. Ammonia, evolved and dried in lime-tower, is collected by downward displacement of air.

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

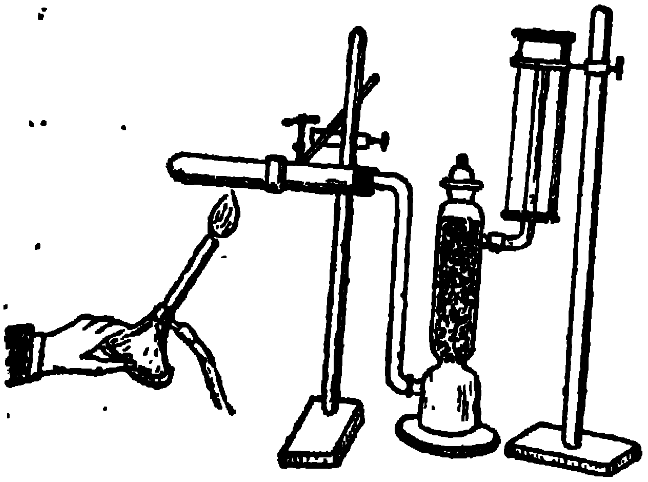


Fig. 145

Properties of ammonia.

Physical :—

It is a (1) colourless gas with a (2) peculiar pungent smell. (3) It is lighter than air and (4) is extremely soluble in water.

Chemical :—

(1) Ammonia is neither a supporter of combustion nor combustible in air. But when the gas is set fire to in an atmosphere of oxygen it burns with a yellowish flame.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

(2) The aqueous solution is alkaline and is soapy to the taste, and so it is supposed to contain ammonium hydroxide, which has not been isolated, for on boiling the aqueous solution, ammonia is completely expelled.

$$NH_3 + H_2O = NH_4OH.$$

The aqueous solution of ammonia can neutralise acids and can precipitate the hydroxides of many metals when added to the solution of their salts.

(3) When ammonia is passed over heated metallic sodium or potassium, the amide of the alkali metal is formed and hydrogen is evolved.

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

(4) Ammonia acts as a reducing agent under certain conditions. Thus, when ammonia is passed over heated copper oxide or lead oxide, metallic copper or lead is formed.

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2.$$

(5) Ammonia in excess reacts with chlorine and is oxidised to nitrogen, the reaction taking place in two stages, *viz.*,

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$
$$6HCl + 6NH_3 = 6NH_4Cl.$$

But with excess of chlorine, nitrogen trichloride is formed.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

Volumetric composition of ammonia is determined by Berthollet's method in the following way :—

A straight graduated eudiometer tube is taken and two platinum wires are sealed into glass near its closed end. It is filled with mercury and inverted over a deep trough of mercury. A certain volume of pure and dry ammonia is collected is the tube by the displacement of mercury and the inside and outside level of mercury in the tube and in the trough are brought to the same level and the volume of ammonia is read off. Let it be 10 c.c. A series of electric sparks are then passed through this volume of ammonia by connecting the two Pt-wires to the terminals of an induction coil. Ammonia is decomposed into nitrogen and hydrogen, and the volume goes on increasing. When there is no further increase in volume, the sparking is stopped, the mercury level is again adjusted and the volume of the mixture is noted. It is found to be 20 c.c. Next, an excess of oxygen is introduced in the eudiometer tube, the volume of the mixture noted after adjusting the mercury level and the mixture exploded by passing a single electric spark through the mixture from an induction coil with the help of the two sealed Pt-wires. Hydrogen and oxygen combine to form steam which condenses into liquid water. The apparatus is cooled, mercury level is again adjusted and the volume of the residual gas noted.

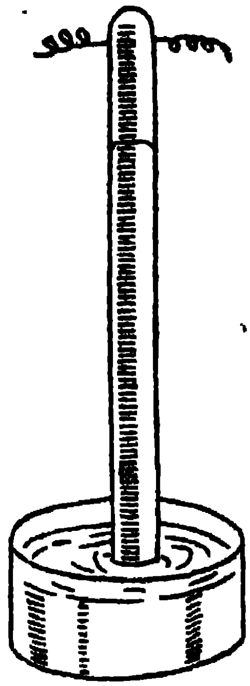


Fig. 146

The following are the readings of the volumes :—
Volume of ammonia taken = 10 c.c.
Volume of N_2+H_2 after sparking = 20 c.c.
Volume after addition of oxygen = 30 c.c.
Volume of the residual gas (N_2 + excess of O_2)
after explosion = 7·5 c.c.
∴ Contraction after explosion with oxygen
(30 − 7·5) c.c. = 22·5 c.c.

This contraction is due to the formation of water ; two-thirds of this contraction is the volume of hydrogen present. Hence volume of hydrogen = $\frac{2}{3}$ × 22·5 c.c. = 15 c.c. and volume of nitrogen = (20 − 15) c.c. or 5 c.c. Thus 10 c.c. of ammonia yield 15 c.c. of hydrogen and 5 c.c. of nitrogen.

Thus from the results of the above experiment it follows that, 1 volume of nitrogen combines with 3 volumes of hydrogen to produce 2 volumes of ammonia.

SECOND PAPER

Q. 1. *Describe, without entering into details, the various methods for the isolation of metals from their ores. Mention at least one example under each head.*

Give a short account of the general properties of metals.

Ans. Sometimes some metals are met with in the *free* state. Then metals are obtained by removing the adhering rocky and siliceous impurities from them. For example, copper has been found in the free state near Lake Superior in America.

Most of the metals, however, are met with in the form of their compounds, such as oxides, sulphides, carbonates etc. In those cases the extraction of the metals is carried out in two steps : (*a*) **Preliminary calcination or roasting**, and (*b*) Subsequent reduction.

(1) **Oxide** :—When the metallic ore is an oxide, it is first calcined to remove volatile impurities associated with it and at the same time to render it porous. The calcined ore is then reduced, the reduction being carried out industrially by heating

the oxide with carbon. This **carbon-reduction process**, as it is called, is the general method followed and is adopted in the cases of Cu, Zn, Pb, Sn, Fe, etc.

$$ZnO + C = Zn + CO.$$
$$SnO_2 + 2C = Sn + 2CO.$$

Sometimes the metal is obtained by simply *heating* the oxide, e.g. in case of oxides of mercury, gold, silver etc. ; or by using an *electric current*, as for example, aluminium is obtained by electrolysis of aluminium oxide at a high temperature, Al_2O_3 being in fused state. Some metallic oxides are reduced by *thermit* process with powdered Al.

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3$$

(2) **Sulphide** :—When the metallic ore is a sulphide, usual procedure is to heat it very strongly in air. Sulphur burns away to SO_2 and the oxide of the metal results. The oxide is then reduced with carbon.

This procedure is adopted with zinc blende, ZnS.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnO + C = Zn + CO.$$

In case of copper, the sulphide ore is freed from iron with which it is associated, then it is bessemerised, whereby partial conversion into oxide takes place and then the oxide and remaining sulphide react to give metallic copper.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

(3) **Carbonate** :—When the ore is a carbonate, it is first calcined in air whereby it yields the oxide of the metal with the removal of CO_2 as gas. The oxide is next reduced with carbon. Calamine or Smithsonite, $ZnCO_3$, is utilised in that way.

$$ZnCO_3(\text{calcined}) = ZnO + CO_2$$
$$ZnO + C = Zn + CO.$$

Spathic iron ore, $FeCO_3$, is also used in the same way for getting the metal.

(4) **Hydroxide** :—When the ore of the metal is a hydroxide, it is strongly heated so as to get the oxide. The oxide is then reduced with carbon.

Limonite, $2Fe_2O_3, 3H_2O$, is utilised in the above way for getting iron.

(5) **Sulphate** :—In the case of the ore being a sulphate, it is first reduced with carbon into the sulphide. The sulphide is next heated strongly in air so as to convert it into oxide. The oxide is then reduced with carbon.

(6) **Halide** :—When the metallic ore is a halide, the metal is extracted

either, (i) by **electrolysis** of the halide in the **fused** state, when the metal is liberated at the cathode and the halogen at the anode. Thus, Na, K, Ca and Mg are obtained by electrolysis of their fused chlorides.

or, (ii) by **fusing** the halide with metallic sodium or potassium. Metallic Mg, Al, Ca can be obtained in this way.

$$MgCl_2 + 2Na = Mg + 2NaCl$$
$$AlCl_3 + 3Na = Al + 3NaCl.$$

General properties of metals :—

Metals generally possess a lustre, called metallic lustre. They are generally good conductors of heat and electricity. They are malleable and ductile, and generally have high specific gravity and reflect light. Metals are electro-positive in character and are liberated at the cathode during electrolysis. They emit a peculiar sound, called metallic clink, when struck with a hammer. They form oxides, by combination with O_2, either at ordinary temperature or when heated, as ZnO, Al_2O_3 etc. which are basic in character but sometimes they are amphoteric. But in some cases higher oxides are found to be acidic. Metals frequently dissolve in dilute mineral acids, giving off hydrogen. They readily combine with halogens, giving their halides.

Q. 2. *2 gms. of a mixture of carbonate, bicarbonate and chloride of sodium gave on gentle heating till no further evolution of gas occurred, 62 c.c. of CO_2 at 26°C and 752 mm. pressure. 1·6 gm. of the same mixture required sufficient HCl obtained from 1·52 gm of NaCl for complete neutralisation.*

Calculate the percentage of carbonate, bicarbonate and chloride in the mixture.

$$Na - 23{\cdot}0,\ C = 12{\cdot}0,\ O - 16{\cdot}0,\ Cl - 35{\cdot}5.$$

Ans. Of the three constituents Na_2CO_3, $NaHCO_3$ and $NaCl$ of the mixture, it is only $NaHCO_3$, which gives CO_2 on heating, according to the equation.

$$\begin{array}{lll} 2\ NaHCO_3 & = Na_2CO_3 + H_2O + & CO_2 \\ 2 \times (23+1+12+48) & & 44 \\ \text{or}\quad 168 & & \end{array}$$

From the above equation

168 grams of sodium bicarbonate, on being decomposed by heating, give 44 grams of carbon dioxide, *i.e.*, 22·4 litres of CO_2 at N.T.P., since molecular weight of any gas expressed in grams occupies 22·4 litres at N.T.P. Now CO_2 evolved from the sodium bicarbonate present in 2 grams of the mixture is 62 c.c. at 26°C. and 752 mm. pressure. Let V be the volume of this CO_2 at N.T.P. Then by Boyle's and Charles' laws, we have

$$\frac{62 \times 752}{273+26} = \frac{V \times 760}{273}.$$

$$\text{when}\quad V = \frac{62 \times 752 \times 273}{299 \times 760}\ \text{c.c.}$$

$$= 56{\cdot}02\ \text{c.c.}$$

Now 22400 c.c. of CO_2 at N.T.P. is evolved from 168 grams of $NaHCO_3$.

$\therefore$ 56·02 c.c. of CO_2 at N.T.P. is given by $\frac{168}{22400} \times 56{\cdot}02$ gram or 0·4202 gram of $NaHCO_3$. Hence 2 grams of the mixture contained 0·4202 gram of $NaHCO_3$.

Therefore, 1·6 grams of the mixture contained $\frac{0{\cdot}4202}{2} \times 1{\cdot}6$ gram or 0·33916 gram of $NaHCO_3$.

Now, from the equation,

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

We know that,

84 grams of sodium bicarbonate require 36·5 grams of HCl for neutralisation. Therefore 0·33616 gram of $NaHCO_3$ will require $\frac{36{\cdot}5}{84} \times 0{\cdot}33616$ gram of HCl, or 0·1461 gram of HCl.

Now, from the equation

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$
$$2 \times 58{\cdot}5 \qquad\qquad 2 \times 36{\cdot}5$$

We know that 2 × 58·5 grams of NaCl yield 2 × 36·5 gms. of HCl. Hence 1·52 gm. of NaCl will yield $\frac{36{\cdot}5}{58{\cdot}5} \times 1{\cdot}52$ gm. of HCl, that is, 0·9484 gm. of HCl, But 0·1461 gm. of HCl is required to neutralise the bicarbonate present in the mixture.

Therefore (0·9484 − 0·1461) gm. or 0·8023 gm. of HCl is used up to neutralise the carbonate of sodium present in the mixture.

From the equation

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$
$$106 \qquad 2 \times 36{\cdot}5$$

We know that 2 × 36·5 gms. of HCl neutralise 106 gms. of Na_2CO_3. Therefore 0·8023 gm. of HCl will neutralise $\frac{106}{2 \times 36{\cdot}5} \times 0{\cdot}8023$ gm. of Na_2CO_3, that is 1·165 gm. of Na_2CO_3.

Hence 1·6 gms, of the mixture supplied contain 1·165 gms. of Na_2CO_3, 0·33616 gm. of $NaHCO_3$ and

[1·6 − (1·165 + 0·33616)] gm.

or, 0·09884 gm. of NaCl.

Therefore, the percentage of $NaHCO_3 = \frac{0{\cdot}33616}{1{\cdot}6} \times 100$

$= 21{\cdot}01.$

" " " $Na_2CO_3 = \frac{1{\cdot}165}{1{\cdot}6} \times 100$

$= 72{\cdot}81.$

" " " $NaCl = \frac{0{\cdot}09884}{1{\cdot}6} \times 100$

$= 6{\cdot}18.$

Q. 3. *Describe an experiment in illustration of each of the following :—*

(*a*) *Burning in an atmosphere of* CO_2. (*b*) *Promotion of a chemical change by light.* (*c*) *Formation of a solid by the mixing of two gases.* (*d*) *Chemical reaction by means of an electric arc.*

Ans. (*a*) A gas-jar is filled with carbon dioxide and then burning magnesium ribbon is introduced into it. The magnesium ribbon continues to burn with separation of soot.

$$2Mg + CO_2 = 2MgO + C.$$

(*b*) A gas jar is filled up with carbon monoxide and another jar is filled up with chlorine, the two jars are then placed mouth to mouth and the gases are thoroughly mixed inside a room. The mixture is then exposed to direct sunlight. CO and Cl_2 combine giving carbonyl chloride or *phosgene gas.*

$$CO + Cl_2 = COCl_2.$$

(*c*) Two gas jars are taken. One of them is filled up with partially dried ammonia gas and the other one with nearly dry hydrogen chloride. The two jars are then placed mouth to mouth. Dense white fumes of ammonium chloride are produced and these gradually settle as solid powder at the bottom and sides of the gas jars.

$$NH_3 + HCl = NH_4Cl.$$

(*d*) Two carbon electrodes are fitted to a glass globe provided with an inlet and an outlet tube. A current of hydrogen is introduced through the inlet tube and air is completely displaced from the glass globe. An arc is then struck between the two carbon pencils. Carbon and hydrogen combine under the influence of electric arc giving acetylene which escapes by the outlet tube.

$$2C + H_2 = C_2H_2.$$

Q. 4. *Give the names and compositions of the chief ores of Zinc. Describe, in brief, the method by which the metal is extracted from the most important of its ores. Explain the chemical reactions involved in its extraction. State the uses of the metal and two of its alloys. How is Zinc detected ?*

Ans. The important ores of zinc are

(1) Calamine or zinc spar or Smithsonite—$ZnCO_3$

(2) Zinc blende or black-jack—ZnS.

Other ores are (3) Red zinc ore—ZnO

(4) Franklinite—(Zn.Fe) O, Fe_2O_3.

The most important ore, zinc blende, ZnS, is found to be associated with galena, (PbS) quartz, sand, etc. To remove these the crushed ore is mixed with a little oil and stirred up with water when zinc blende rises to the surface and is thus separated from galena, sand, etc. which remain at the bottom. The carbonate ore, zinc spar, is also used for the purpose of extracting the metal without preliminary concentration.

The process of extraction consists of two operations, namely, first, the conversion of the ore into oxide of zinc, by roasting; and secondly, the reduction of the oxide by means of coal at a high temperature.

Purified ZnS is roasted in multiple hearth furnace and is oxidised to ZnO. Care is taken to see that it is transformed as completely as possible into ZnO and not into $ZnSO_4$.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The roasting of natural carbonate is readily accomplished, this compound merely giving off its CO_2 at a high temperature—

$$ZnCO_3 = ZnO + CO_2.$$

The roasted ore is then mixed with powdered coke and introduced in fire-clay retorts, which are strongly heated; ZnO is reduced at or above 1000°C. to zinc, which distils off being volatile :

$$ZnO + C = Zn + CO.$$

The *Belgian retorts* are fire-clay tubes closed at one end, with iron tubes as receivers in which zinc condenses and solidifies. *Silesian retorts* are muffle furnaces with receivers of iron luted with fire-clay. About 10%—25% of Zn is lost due to oxidation of zinc and formation of zinc-dust, etc.

The chemical reactions involved in the extraction of zinc are : roasting of the ore with the production of its oxide and subsequent reduction of the oxide with carbon. Here sufficient amount of carbon is added to form carbon monoxide and taking care that no carbon dioxide is formed, for in that case, the liberated zinc vapour will be oxidised during codensation. Also much higher temperature than the boiling point of zinc is employed for preventing the formation of CO_2.

Uses of zinc.—Zinc is used for galvanising iron sheets, for the manufacture of vats, tanks and pipes, for the electrodes of electric cells, in the extraction of gold and silver, for the production of hydrogen and as a reducing agent in the laboratory, specially in the form of zinc dust.

Important alloys of zinc are ordinary brass, Dutch metal, German silver and bronze. Brass is used for manufacture of utensils, German silver is used for preparation of artistic vessels as also for ordinary utensils and in the preparation of cheap ornaments.

Zinc can be detected in its compounds both by dry tests and wet tests applied on them.

(1) Compounds of zinc, when mixed with Na_2CO_3 and heated on charcoal under the blowpipe flame, leave an incandescent residue which is *yellow* when hot, but becomes *white* on cooling. On moistening the white residue with a drop or two of cobalt nitrate solution and heating again under the oxidising blowpipe flame, a *green* mass is obtained (Rinman's green).

(2) When NaOH, KOH or NH_4OH solution is added to a solution of a zinc salt in small amount, a white precipitate of $Zn(OH)_2$ is produced. But the precipitate dissolves in excess of the alkali.

(3) $(NH_4)_2S$ solution, on being added to a zinc salt solution, yields a white precipitate of ZnS.

Q. 5. *Describe and explain, with equation what happens when :—*

(*a*) *chlorine is passed over molten tin scrap,*

(*b*) *a hot solution of ferric chloride is treated with stannous chloride solution,*

(*c*) *lead dioxide is heated with concentrated sulphuric acid,*

(*d*) *carbon dioxide is passed into a solution of sodium aluminate,*

(*e*) *ammonia is added to any mercurous salt.*

Ans. (*a*) Stannic chloride is formed, which can be volatilised by heat and can be condensed to a fuming liquid by cooling.

$$Sn + 2Cl_2 = SnCl_4.$$

In this case tin is completely oxidised to the stannic state.

(*b*) Ferric chloride solution (yellow) is reduced to ferrous chloride solution (colourless) by the reducing action of stannous

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

(*c*) Oxygen is evolved as gas and lead sulphate (insoluble) is formed at first, a portion of which dissolves in excess of hot conc. H_2SO_4.

$$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + O_2 + 6H_2O.$$

(*d*) When CO_2 is passed through sodium aluminate solution heated at 50° – 60°C, aluminium hydroxide is precipitated and sodium carbonate is formed in solution.

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3.$$

(*e*) When ammonia is added to any mercurous salt, a black residue is obtained, containing finely divided mercury and amido-mercuric salt of the acid radical in combination with mercury.

$$\begin{array}{l} Hg_2(NO_3)_2 + 2NH_3 = NH_2HgNO_3 + Hg \\ \quad \text{soluble} \qquad\qquad\qquad + NH_4NO_3. \\ Hg_2Cl_2 + 2NH_3 = NH_2HgCl + Hg + NH_4Cl. \\ \text{Insoluble.} \end{array}$$

Q. 6. *Write a short essay on Mendeleeff's periodic classification of elements. Discuss its merits and demerits.*

Ans. In 1869 the Russian Chemist Mendeleeff discovered that when the elements are arranged in the order of increasing Atomic weights, their properties vary from member to member in a definite way, but return more or less to the same value at fixed points in the series.

Mendeleoff arranged the elements in a table in the order of their increasing atomic weights, the table being called the *periodic table* or the *periodic system.* The original table, however, has undergone many modifications with the discovery of new data. Such a new table is appended herewith. In the table the elements are found to be arranged in horizontal series in such a fashion that when elements with similar chemical

PERIODIC TABLE

(With **Atomic numbers** written above and **Atomic weights** written by the side of symbols).

Pe-ri-ods.	Group I R_2O RH A B	Group II R_2O_2 RH_2 A B	Group III R_2O_3 RH_3 A B	Group IV R_2O_4 RH_4 A B	Group V R_2O_5 RH_3 A B	Group VI R_2O_6 RH_2 A B	Group VII R_2O_7 RH A B	Group VIII R_2O_8→forml. of oxides →forml. of hydrides A	Group O Or Gr. VIII B
1							1 H 1 008		2 He 4
2	3 Li 6·94	4 Be 9·02	5 B 10·82	6 C 12	7 N 14·01	8 O 16	9 F 19		10 Ne 20
3	11 Na 23	12 Mg 24·3	13 Al 26 97	14 Si 28 06	15 P 31·04	16 S 32	17 Cl 35·46		18 A 39·0
4	19 K 39·1 29 Cu 63·5	20 Ca 40 30 Zn 65 3	21 Sc 45·1 81 Ga 70	22 Ti 48·1 32 Ge 72·5	23 V 51 33 As 74 9	24 Cr 52 34 S 79·2	25 Mn 54 9 35 Br 79 9	26 27 28 Fe 55·8 Co 58·9 Ni 58·6	36 Kr 83 7
5	37 Rb 85·4 47 Ag 107 8	38 Sr 87·63 48 Cd 112	39 Y 88 9 49 In 114·8	40 Zr 91·20 50 Sn 119	41 Nb 92 9 51 Sb 121·76	42 Mo 96 52 Te 127·6	43 Tc 97 8 53 I 126·9	44 45 46 Ru 101·7 Rh 103 Pd 106	54 Xe 131
6	55 Cs 132·9 79 Au 197·2	56 Ba 137·37 80 Hg 200·6	57 La 139 58—71 Rare-earths* 81 Tl 204	72 Hf 178·6 82 Pb 207·2	73 Ta 180·8 83 Bi 209	75 W 184 84 Po 210	75 Re 186·3 85 At 210	76 77 78 Os 191 Ir 193 Pt 195	86 Rn 222
7	87 Fr 223·1	88 Ra 226	89 Ac 227	90 Th 232·12	91 Pa 231	92 U 238·14			

* Rare-earth.—58 Ce, 59 Pr, 60 Nd, 61 Pm, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho. 68 Er, 69 Tm, 70 Yb, 71 Lu

properties are reached, they are arranged in the same vertical column. The horizontal series are called *periods*, and the vertical columns are called *groups*. The periods are divided into *short* and *long*, according to the number of elements present in them. It is found from the table appended that the 1st period consists of only two elements, Hydrogen and Helium. The 2nd period contains 8 elements from Lithium to Neon and the 3rd period also consists of 8 elements from Sodium to Argon. The 2nd and 3rd periods are called *short periods*. Then comes the 4th period with 18 elements starting from Potassium and ending in Krypton ; similarly the 5th period consists of 18 elements starting from Rubidium and ending in Xenon. These 4th and 5th periods are known as *long periods*. The 6th period contains 32 elements, starting from Cæsium and ending in Radon and comprising in itself all the fifteen rare-earth elements. This 6th period is called a *very long period* or a *monster period*. The 7th period is fragmentary and it consists of only six radio-active elements, of which the first one is an analogue of the alkali metals. The vertical groups now are nine in number, marked O (zero) to VIII. The group O includes all the inert gases like Helium, Neon, Argon, Krypton, Xenon and Radon, discovered in atmospheric air long after the construction of the periodic table by Mendeleeff. These gases show no combining capacity and so their valency in zero. Groups are subdivided by Mendeleeff into two sub-groups, subgroup A and subgroup B. The elements in the A subgroup resemble one another more closely than they resemble elements of B subgroup, which again have so much similarity among themselves. This subgroup A of group I includes the alkali metals, and subgroup B of group I includes the coinage metals (copper, silver, gold). The alkali metals resemble one another very closely, but they show wide divergence in properties from those of coinage metals ; the coinage metals again show similarity among themselves.

The group number is found to correspond to the highest valency of the elements in the group with regard to oxygen.

By arranging the elements in the above fashion, periodicity in both physical and chemical properties is at once seen. Such physical properties as atomic volume (atomic weight ÷ specific gravity), melting-point, boiling-point, electrical conductivity etc., when plotted against the atomic weight in a graph perfectly periodic curves, showing waxing and waning at regular intervals, are obtained. In those graphs, similar elements are found to occupy similar positions.

Similarly such typical chemical properties as valency and electro-chemical character of elements are found also to be periodic in nature. Thus, Lithium has a valency I with regard to hydrogen, NaH being the hydride formed by it. Similarly hydrogen valency rises upto 4 in group IV and then falls regularly to I again in group VII and then becomes zero in group O. This is repeated in the 2nd period.

The oxygen-valency is found to start from I in group I and go upto eight in group VIII and then falls to zero in group O and this regularity is seen in each period. The triads occurring in group VIII were named by Mendeleeff "*transitional elements*", but this term "transitional elements" has now been applied to all elements starting from Scandium and ending in zinc in the 1st long period, from Yttrium to Cadmium in 2nd long period, and from Lanthanum to Mercury in the very long period. Hence Mendeleeff stated his Periodic Law as follows :— "The physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights."

Merits of the Periodic Classification :—

(1) *It has systematised the study of Inorganic Chemistry* by rendering the study of nearly 92 diverse elements into a study of nine vertical columns.

(2) *It has helped in the correction of doubtful atomic weights.* One example will make this clear. The equivalent weight of Indium was found to be 38. Its atomic weight was taken as 2 × 38 = 76, by considering it to be bivalent. In that case Indium was to be placed between Arsenic and Selenium. But there was no room for such an element there. Mendeleeff, judging from its properties, suggested that Indium should have an atomic weight 3 × 38 = 114, which would place it between cadmium and Tin, where it fits very well. The subsequent determination of the atomic heat of Indium and thence its atomic weight corroborated this change and the correct atomic weight of Indium is taken as 114 and not 76.

(3) *It has helped in the predition of new elements.* At the time when the Periodic table was first constructed, Mendeleeff left three gaps in the table in the first long period in positions where Scandium, Gallium and Germanium now occur. To the unknown elements which were stated to occupy those positions, Mendeleeff gave the names *eka-boron*, eka-*aluminium* and *eka-silicon* and from the known properties of the neighbouring elements of the series and also of those situated nearest in the same family, he predicted some of the prominent properties that would probably be possessed by these elements. These predictions came out to be true when in 1875 Lecoq de Boisbaudran discovered Gallium tallying in properties with eka-aluminium. Discovery of Scandium (Nilson, 1879) and Germanium (Winkler, 1886), when properties were found to accord closely with those of eka-boron and eka-silicon respectively formed an additional demonstration of the truth of the Periodic Law.

(4) *It has helped in the furtherance of researeh in Chemistry.*

Demerits of the Periodic Classification :—

I. The position of Hydrogen is yet open to discussion. It is monovalent and so can be placed either in Group I with the alkali metals or in Group VII with the halogens. The only argument in favour of placing Hydrogen with the alkali metals is that it is an electropositive element like alkali metals. Arguments in favour of placing Hydrogen in Group VII with the halogens are :—(1) Like the first two members of the family, *viz.*, F and Cl, it is a gas. (2) Like the halogens, it has di-atomic molecules. (3) It may be replaced, atom for atom, from organic compounds by the halogens. (4) Just as the metals form halides with the halogens, similarly alkali metals and the alkaline earth metals form definite hydrides with Hydrogen and in these hydrides Hydrogen behaves as an electronegative element. (5) If Hydrogen be placed in Group VII, the difference between the at. wts. of Hydrogen and its next congener Fluorine is 18 which is nearly the usual difference between the atomic weights of two successive elements in the same group in the first two periods ; but this sequence is broken if it be placed in Group I, a difference of only 6 being observed. To avoid these difficulties Hydrogen has been placed at head of the table in a separate series by itself.

II. In the case of some elements, the atomic weight sequence is broken ; thus in three sets

(*a*) Argon (39·9) and Potassium (39·0)
(*b*) Cobalt (58·9) and Nickel (58·6)
(*c*) Tellurium (127·5) and Iodine (126·2)

Atomic weight sequence is reversed in those cases on chemical grounds.

III. There are fifteen rare-earth elements for which appropriate places have not been found and they are placed together in one position in Group III.

IV. The periodic classification according to atomic weights overlooks certain chemical analogies. For examples :—

(*a*) Copper, Silver and Gold have very little analogies with Sodium, Potassium etc. and yet they have been placed in the same group with the alkali metals. Similarly, Manganese has been placed in the same group with the Halogens.

(b) Copper and Mercury, Silver and Thallium, Barium and Lead, which appear to be chemically similar, are, placed in separate groups.

Q. 7, *What is dialysis ? Describe an experiment to illustrate it.*

How will you prepare colloidal silicic acid and silica from sodium silicate ?

Ans. *Dialysis.*—Dialysis is the process by which a crystalloid is separated from a colloid by mean of a semi-permeable membrane which is capable of allowing the crystalloid molecules to pass through it, but not the colloid particles.

Graham found that certain substances like gum, albumen, silicic acid, *etc.*, in solution cannot pass practically through parchment, animal bladder, *etc.*, whereas certain other substances like hydrochloric acid, common salt, nitre, *etc.*, in solution readily pass through the parchment, animal bladder, etc.

Thus, a shallow bell jar open at both ends, but fitted with a piece of parchment paper or bladder at one end is kept partly immersed in water in another jar. Into the bell jar aqueous solution of potassium iodide is taken along with certain amount of starch also in solution. A little of this mixed solution when treated with chlorine water turned blue. After a time it is found that potassium iodide has passed into the outer jar but not particles of starch present in the solution. It is proved by adding chlorine water to water present in the outer jar which turns brown due to liberation of iodine from KI.

The apparatus shown in the adjoining figure and used in the experiment is called a dialyser, and this process of separation of a colloid like starch from a crystalloid like potassium iodide is called dialysis.

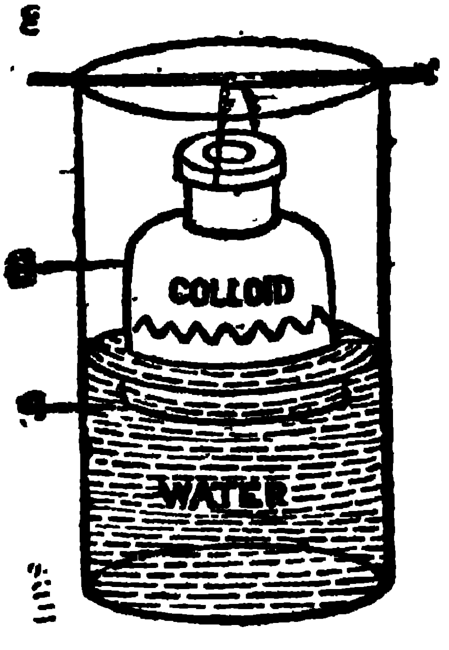


Fig. 147

Preparation of colloidal silicic acid from sodium silicate :—Sodium silicate solution is carefully added to an excess of conc. HCl, when silicic acid is formed. But it remains in *colloidal* solution. The solution also contains NaCl and HCl.

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3.$$

The mixture is placed in a dialyser, which is placed suspended in water. The smaller sized molecules and ions of HCl and NaCl pass through the pores of the membrane, while the bigger sized particles of colloidal silicic acid remain behind in the dialyser in colloidal solution.

Silica from sodium silicate :—Solid sodium silicate is taken in a basin and conc. HCl is added to it. The mixture is heated on an asbestos board till a solid residue is left behind. This solid residue is sintered at 150°C with constant stirring with a glass rod for about 15 minutes. The basin is then removed from the asbestos board and cooled to room temperature. The solid residue is then boiled with water and filtered. Sodium chloride dissolves and is removed in solution. The residue on filter paper is silica, SiO_2. It is collected and dried.

$$Na_2SiO_3 + 2HCl = 2NaCl + SiO_2 + H_2O.$$

Q. 8. *Define and illustrate the following :—*

Decomposition, dissociation, electrochemical equivalent, efflorescence and deliquescence.

Ans. Decomposition is a general term. It signifies permanent breaking down of a compound into simpler components, which do not unite again under changed condition.

Thus, ammonium nitrate decomposes on heating into nitrous oxide and water, but under no changed condition nitrous oxide and water combine to form ammonium nitrate.

$$NH_4NO_3 = N_2O + 2H_2O.$$

—**Dissociation** is a temporary splitting up of molecules into simpler molecules or atoms which reunite under different experimental conditions, the splitting taking place in such a fashion that dynamic equilibrium is set up under all changed conditions between undecomposed molecule and the simpler compounds formed from it,

Thus, on heating, NH_4Cl dissociates into NH_3 and HCl and on cooling NH_4Cl is formed back, but during heating an equilibrium condition is set up depending on temperature, when rate of decomposition and of recombination of NH_3 and HCl is found to balance.

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

Electro-chemical equivalent :—The electro-chemical equivalent of an element is that weight of it in grams. which is liberated by one coulomb of electricity, *i. e.*, one ampere of electric current flowing for one second.

The electro-chemical equivalent of hydrogen is 0·0000104 and the electro-chemical equivalent of any other element is, from Faraday's second law of electrolysis, the chemical equivalent of that element multiplied by the electro-chemical equivalent of H_2.

Efflorescence is the phenomenon shown by some crystallohydrates of slowly losing water of crystallisation at the ordinary temperature when left exposed to air. Thus, crystals of washing soda, $Na_2CO_3, 10H_2O$, when left exposed to air at the ordinary temperature, loses 9 molecules of water of crystallisation and falls to powder giving rise to the monohydrate, Na_2CO_3,H_2O. Washing soda, therefore, exhibits the phenomenon of efflorescence.

Deliquescence is the phenomenon shown by some crystalline solids of absorbing moisture from air, when they are kept exposed to air. These solids, under the condition mentioned, become first moist and ultimately turn into liquid. Thus solid calcium chloride or magnesium chloride, on exposure to air, turns moist and then melt in the water abstracted from air. Thus calcium chloride and magnesium chloride are said to show the phenomenon of deliquescence.